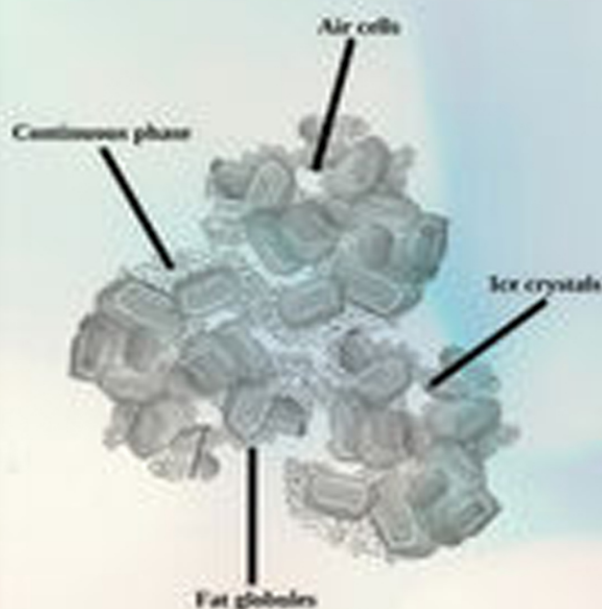
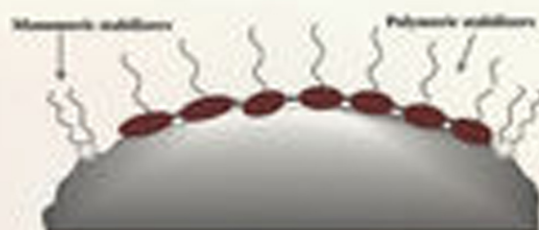
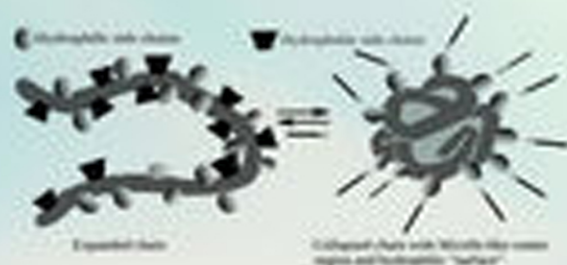


DREW MYERS

SURFACTANT SCIENCE AND TECHNOLOGY

FOURTH EDITION



WILEY

Surfactant Science and Technology

Surfactant Science and Technology

Fourth Edition

Drew Myers
Industrial Consultant
Rio Tercero, Cordoba, Argentina

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To Martin, Violeta, and Victoria – you light up my life!!

Contents

Preface xv

1	An Overview of Surfactant Science and Technology	1
1.1	A Brief History of Surfactant Science and Technology	3
1.2	Surfactants in the Modern World	5
1.3	The Economics of Surfactant Science and Technology	8
1.4	The Near-Term Economic and Technological Future for Surfactants	10
1.5	Surfactants in the Environment	11
1.6	A Surfactant Glossary	13
2	The Classification of Surfactants	17
2.1	The Basic Structure of Amphiphilic Molecules	17
2.2	A Systematic Classification of Surfactants	19
2.2.1	Surfactant Solubilizing Groups	19
2.2.2	Making a Choice	21
2.3	The Generic Anatomy of Surfactants	21
2.3.1	The Many Faces of Dodecane	22
2.3.2	Surfactant Solubilizing Groups	25
2.3.3	Common Surfactant Hydrophobic Groups	26
2.3.3.1	The Natural Fatty Acids	27
2.3.3.2	Saturated Hydrocarbons or Paraffins	28
2.3.3.3	Olefins	28
2.3.3.4	Alkyl Benzenes	29
2.3.3.5	Alcohols	29
2.3.3.6	Alkyl Phenols	30
2.3.3.7	Polyoxypropylenes	30
2.3.3.8	Fluorocarbons	31
2.3.3.9	Silicone Surfactants	32
2.3.3.10	Miscellaneous Biological Structures	32
2.4	The Systematic Classification of Surfactants	33
2.5	Anionic Surfactants	34
2.5.1	Sulfate Esters	35
2.5.1.1	Fatty Alcohol Sulfates	36
2.5.1.2	Sulfated Fatty Acid Condensation Products	36

2.5.1.3	Sulfated Ethers	37
2.5.1.4	Sulfated Fats and Oils	38
2.5.2	Sulfonic Acid Salts	39
2.5.2.1	Aliphatic Sulfonates	39
2.5.2.2	Alkyl Aryl Sulfonates	40
2.5.2.3	α -Sulfocarboxylic Acids and Their Derivatives	42
2.5.2.4	Miscellaneous Sulfo-Ester and Amide Surfactants	43
2.5.2.5	Alkyl Glyceryl Ether Sulfonates	46
2.5.2.6	Lignin Sulfonates	46
2.5.3	Carboxylate Soaps and Detergents	46
2.5.4	Phosphoric Acid Esters and Related Surfactants	48
2.6	Cationic Surfactants	49
2.7	Nonionic Surfactants	51
2.7.1	Polyoxyethylene-Based Surfactants	51
2.7.2	Derivatives of Polyglycerols and Other Polyols	52
2.7.3	Block Copolymer Nonionic Surfactants	54
2.7.4	Miscellaneous Nonionic Surfactants	54
2.8	Amphoteric Surfactants	55
2.8.1	Imidazoline Derivatives	56
2.8.2	Surface-Active Betaines and Sulfobetaines	57
2.8.3	Phosphatides and Related Amphoteric Surfactants	58
3	Surfactant Chemical Structures: Putting the Pieces Together	61
3.1	Surfactant Building Blocks	61
3.2	A Surfactant Family Tree	63
3.2.1	The Many Faces of Dodecane	63
3.3	Common Surfactant Hydrophobic Groups	66
3.3.1	The Natural Fatty Acids	67
3.3.2	Paraffins or Saturated Hydrocarbons	67
3.3.3	Olefins	67
3.3.4	Alkylbenzenes	68
3.3.5	Alcohols	69
3.3.6	Alkylphenols	70
3.3.7	Polyoxypropylene	70
3.3.8	Fluorocarbons	70
3.3.9	Silicone-Based Surfactants	72
3.3.10	Nonchemically Produced, a.k.a. "Natural" Surfactants	74
4	Natural Surfactants and Biosurfactants	75
4.1	What Makes a Surfactant "Natural"?	76
4.2	Surfactants Based on a Natural Sugar-Based Polar Head Groups	78
4.3	Biosurfactants	80
4.3.1	Biosurfactants as Nature Makes Them	80
4.3.2	Properties of Biosurfactants	81
4.3.3	Biosurfactant Classification	83
4.3.4	Some Aspects of Biosurfactant Production	84
4.3.5	Some Factors Affecting Biosurfactant Production	85

4.4	Biosurfactant Applications	87
4.5	Potential Limitations on the Commercial Use of Biosurfactants	90
4.6	Some Opportunities for Future Research and Development	90
4.7	Some Observations About the Future of Biosurfactants	90
5	Fluid Surfaces and Interfaces	93
5.1	Molecules at Interfaces	95
5.2	Interfaces and Adsorption Phenomena	97
5.2.1	A Thermodynamic Picture of Adsorption	97
5.2.2	Surface and Interfacial Tensions	99
5.2.3	The Effect of Surface Curvature	101
5.2.4	The Surface Tension of Solutions	102
5.2.5	Surfactants and the Reduction of Surface Tension	103
5.2.6	Efficiency, Effectiveness, and Surfactant Structure	105
6	Surfactants in Solution: Self-Assembly and Micelle Formation	115
6.1	Surfactant Solubility	116
6.2	The Phase Spectrum of Surfactants in Solution	119
6.3	The History and Development of Micellar Theory	123
6.3.1	Manifestations of Micelle Formations	124
6.3.2	Thermodynamics of Dilute Surfactant Solutions	127
6.3.3	Classical Theories of Micelle Formation	128
6.3.4	Free Energy of Micellization	129
6.4	Molecular Geometry and the Formation of Association Colloids	130
6.5	Experimental Observations of Micellar Systems	133
6.5.1	Micellar Aggregation Numbers	133
6.5.2	The Critical Micelle Concentration	135
6.5.3	The Hydrophobic Group	135
6.5.4	The Hydrophilic Group	143
6.5.5	Counterion Effects on Micellization	145
6.5.6	The Effects of Additives on the Micellization Process	146
6.5.6.1	Electrolyte Effects on Micelle Formation	147
6.5.6.2	The Effect of pH	148
6.5.6.3	The Effects of Added Organic Materials	149
6.5.7	The Effect of Temperature on Micellization	151
6.6	Micelle Formation in Mixed Surfactant Systems	153
6.7	Micelle Formation in Nonaqueous Media	154
6.7.1	Aggregation in Polar Organic Solvents	155
6.7.2	Micelles in Nonpolar Solvents	155
7	Beyond Micelles: Higher Level Self-Assembled Aggregate Structures	161
7.1	The Importance of Surfactant Phase Information	161
7.2	Amphiphilic Fluids	163
7.2.1	Liquid Crystalline, Bicontinuous, and Microemulsion Structures	163
7.2.2	“Classical” Liquid Crystals	165
7.2.3	Liquid Crystalline Phases in Simple Binary Systems	166
7.3	Temperature and Additive Effects on Phase Behavior	170

7.4	Some Current Theoretical Analyses of Novel Mesophases	171
7.5	Vesicles and Bilayer Membranes	171
7.5.1	Vesicles	173
7.5.2	Polymerized Vesicles	174
7.6	Biological Membranes	176
7.6.1	Some Biological Implications of Mesophases	176
7.6.2	Membrane Surfactants and Lipids	177
7.7	Microemulsions	179
7.7.1	Surfactants, Co-surfactants, and Microemulsion Formation	183
7.7.1.1	Ionic Surfactant Systems	183
7.7.1.2	Nonionic Surfactant Systems	184
7.7.2	Applications	185
8	Surfactant Self-Assembled Aggregates at Work	187
8.1	Solubilization in Surfactants Micelles	188
8.1.1	The “Geography” of Solubilization in Micelles	189
8.1.2	Surfactant Structure and the Solubilization Process	191
8.1.3	Solubilization and the Nature of the Additive	194
8.1.4	The Effect of Temperature on Solubilization Phenomena	196
8.1.5	The Effects of Nonelectrolyte Solutes	197
8.1.6	The Effects of Added Electrolyte	198
8.1.7	Miscellaneous Factors Affecting Micellar Solubilization	199
8.1.8	Hydrotropes	199
8.2	Micellar Catalysis	201
8.2.1	Micellar Catalysis in Aqueous Solution	201
8.2.2	Micellar Catalysis in Nonaqueous Solvents	203
9	Polymeric Surfactants and Surfactant–Polymer Interactions	205
9.1	Polymeric Surfactants and Amphiphiles	205
9.2	Some Basic Chemistry of Polymeric Surfactant Synthesis	207
9.2.1	The Modification of Natural Cellulosic Materials, Gums, and Proteins	207
9.2.2	Synthetic Polymeric Surfactants	208
9.3	Polymeric Surfactants at Interfaces: Structure and Methodology	213
9.4	The Interactions of “Normal” Surfactants with Polymers	214
9.4.1	Surfactant–Polymer Complex Formation	215
9.4.2	Nonionic Polymers	218
9.4.3	Ionic Polymers and Proteins	219
9.5	Polymers, Surfactants, and Solubilization	222
9.6	Surfactant–Polymer Interactions in Emulsion Polymerization	223
10	Emulsions	225
10.1	The Liquid–Liquid Interface	226
10.2	General Considerations of Emulsion Stability	227
10.2.1	The Lifetimes of Typical Emulsions	230
10.2.2	Theories of Emulsion Stability	232
10.3	Emulsion Type and the Nature of the Surfactant	233
10.4	Surface Activity and Emulsion Stability	235

10.5	Mixed Surfactant Systems and Interfacial Complexes	239
10.6	Amphiphile Mesophases and Emulsion Stability	242
10.7	Surfactant Structure and Emulsion Stability	245
10.7.1	The Hydrophile–Lipophile Balance (HLB)	245
10.7.2	Phase Inversion Temperature (PIT)	250
10.7.3	Application of HLB and PIT in Emulsion Formulation	251
10.7.4	The Effects of Additives on the “Effective” HLB of Surfactants	253
10.8	Multiple Emulsions	254
10.8.1	Nomenclature for Multiple Emulsions	254
10.8.2	Preparation and Stability of Multiple Emulsions	254
10.8.3	Pathways for Primary Emulsion Breakdown	255
10.8.4	The Surfactants and Phase Components	256
11	Foams and Liquid Aerosols	259
11.1	The Physical Basis for Foam Formation	260
11.2	The Role of Surfactant in Foams	263
11.2.1	Foam Formation and Surfactant Structure	266
11.2.2	Amphiphilic Mesophases and Foam Stability	268
11.2.3	The Effects of Additives on Surfactant Foaming Properties	269
11.3	Foam Inhibition	271
11.4	Chemical Structures of Antifoaming Agents	272
11.5	A Summary of the Foaming and Antifoaming Activity of Additives	273
11.6	The Spreading Coefficient	274
11.7	Liquid Aerosols	276
11.7.1	The Formation of Liquid Aerosols	276
11.7.1.1	Spraying and Related Mechanisms of Mist and Fog Formation	276
11.7.1.2	Nozzle Atomization	277
11.7.1.3	Rotary Atomization	278
11.7.2	Aerosol Formation by Condensation	279
11.7.3	Colloidal Properties of Aerosols	282
11.7.3.1	The Dynamics of Aerosol Movement	282
11.7.3.2	Colloidal Interactions in Aerosols	284
12	Solid Surfaces: Adsorption, Wetting, and Dispersions	287
12.1	The Nature of Solid Surfaces	287
12.2	Liquid Versus Solid Surfaces	290
12.3	Adsorption at the Solid–Liquid Interface	291
12.3.1	Adsorption Isotherms	292
12.3.2	Mechanisms of Surfactant Adsorption	293
12.3.2.1	Dispersion Forces	294
12.3.2.2	Polarization and Dipolar Interactions	295
12.3.2.3	Electrostatic Interactions	296
12.3.3	The Electrical Double Layer	297
12.4	The Mechanics of Surfactant Adsorption	298
12.4.1	Adsorption and the Nature of the Adsorbent Surface	299
12.4.2	Nonpolar, Hydrophobic Surfaces	299
12.4.3	Polar, Uncharged Surfaces	300

12.4.4	Surfaces Having Discrete Electrical Charges	301
12.5	Surfactant Structure and Adsorption from Solution	303
12.5.1	Surfaces Possessing Strong Charge Sites	303
12.5.2	Adsorption by Uncharged, Polar Surfaces	306
12.5.3	Surfactants at Nonpolar, Hydrophobic Surfaces	306
12.6	Surfactant Adsorption and the Character of Solid Surfaces	307
12.7	Wetting and Related Phenomena	308
12.7.1	Surfactant Manipulation of the Wetting Process	311
12.7.2	Some Practical Examples of Wetting Control By Surfactants	314
12.7.3	Detergency and Soil Removal	314
12.7.4	The Cleaning Process	314
12.7.5	Soil Types	315
12.7.6	Solid Soil Removal	316
12.7.7	Liquid Soil Removal	317
12.7.8	Soil Re-deposition	318
12.7.9	Correlations of Surfactant Structure and Detergency	319
12.7.10	Nonaqueous Cleaning Solutions	320
12.8	Suspensions and Dispersions	321

13 Special Topics in Surfactant Applications 323

13.1	Surfactants in Foods	323
13.1.1	The Legal Status of Surfactants in Food Products	324
13.1.2	Typical Food Emulsifier Sources	324
13.1.3	Chemical Structures of Some Important Food Emulsifiers	326
13.1.3.1	Monoglycerides	326
13.1.3.2	Derivatives of Monoglycerides	327
13.1.3.3	Derivatives of Sorbitol	329
13.1.3.4	Polyhydric Emulsifiers	330
13.1.3.5	Polyglycerol Esters	331
13.1.3.6	Sucrose Esters	331
13.1.3.7	Anionic Food Emulsifiers	332
13.1.3.8	Lecithin	333
13.2	Some Important Functions of Surfactants in Food Products	334
13.2.1	Emulsifiers as Crystal Modifiers in Food	335
13.2.2	Bakery Products	337
13.2.2.1	Anti-staling Agents	338
13.2.2.2	Starch–Emulsifier Complexation	339
13.2.2.3	Dough Strengtheners	340
13.2.2.4	Aerating Agents	341
13.2.3	Emulsifier Use in Dairy and Nondairy Substitutes	342
13.2.3.1	What Makes Milk “Milk”?	343
13.2.3.2	Surfactant Uses in Cheeses and Cheese Substitutes	344
13.2.3.3	Surfactant Use in Deserts and Yogurts	344
13.2.3.4	Butter and Margarine	344
13.2.3.5	Whipped Cream and Nondairy Whipped Toppings	345
13.2.3.6	Dairy Drinks	347
13.2.3.7	Ice Cream	347

13.2.3.8	Coffee Whiteners	348
13.2.4	Protein Emulsifiers in Foods	349
13.2.4.1	Proteins as Foam Stabilizers	351
13.2.4.2	Proteins as Emulsifying Agents	352
13.2.4.3	Protein–Low Molecular Weight Emulsifier Interactions	353
13.3	Pharmaceutical and Medicinal Applications	354
13.4	Petroleum and Natural Gas Extraction	355
13.4.1	Enhanced Oil Recovery	356
13.4.2	Hydraulic Fracturing or “Fracking”	358
13.5	Paints and Surface Coatings	359
13.5.1	Interfaces in Paints and Coatings	360
13.5.2	Wetting and Dispersing Additives	361
13.5.3	Wetting Agents	363
13.5.4	Dispersing Agents	363
13.5.5	Surface Wetting with Silicone Surfactants	366
14	“Multiheaded” Amphiphiles: Gemini and Bolaform Surfactants	369
14.1	Two (or More) Can Be Better Than One	369
14.1.1	Structural Characteristics of Gemini Surfactants	370
14.1.2	Some Synthetic Pathways to Gemini Structures	371
14.1.3	Important Surfactant Properties of Gemini Surfactants	372
14.1.4	Some “Outside the Box” Potential Applications of Gemini Surfactants	375
14.2	Bolaform Surfactants	377
14.3	Chemical Structures and Self-Assembly Patterns	380
	Chapter Bibliographies	381
	Index	389

Preface

Like life in general, when a book reaches the level of a fourth edition, it will be guaranteed that some things have changed, while others remain essentially the same. That general rule holds true with the subject of surface-active materials or surfactants. In the previous three editions, the basic concepts of the actions of materials covered by this important scientific and technological subject area largely remain the same, but obviously with numerous “tweaks” brought about by advances in the techniques available for the study and theoretical understanding of new materials and applications. The basic improvements in understanding of the subject achieved in the years since publication of the third edition have added greatly to our understanding of the molecular nature of the interactions of surface-active materials and the consequences their presence can have on system characteristics and performance. Perhaps more importantly, new classes of materials have significantly broadened the range of chemical species that are available for application in the “traditional” uses of surfactants and newer areas related to microbiology, health care and related sciences, environmental sciences, and the search for “greener” uses. Without changing the fundamental philosophy and goals of the previous editions, this fourth edition was prepared with four major ideas in mind: (i) to maintain current the basic contents of the work in terms of the concepts of the actions of surfactants, (ii) to maintain the “readability” of the book for nonspecialists, (iii) to improve the book’s utility as a source of basic concepts concerning surfactants and their applications, and (iv) to introduce new classes and sources of surfactants not specifically covered previously. To achieve the last goal, new chapters have been included related to so-called “natural” surfactants resulting from biologically derived sources discussed in Chapter 4 and new molecular forms containing multiple surfactant structures in a single molecule. The latter materials include the so-called “gemini” and “bolaform” surfactants discussed in Chapter 14. A new chapter, Chapter 13, has also been included that tries to introduce more specific information on surfactant application and actions in specific application areas. Obviously, those new additions are limited in scope due to space limitations and represent rather simple overviews. However, it is hoped that they will serve to highlight what is happening now and perhaps inspire interest in new possibilities.

To that end, some chapters have been condensed or combined, while new chapters have been added to emphasize more practical aspects of surfactant science in applied technical fields. As in past editions, the general Bibliography provided for each chapter should serve as a useful guide to more detailed coverage for the interested reader. Hopefully, the material presented will continue to serve as a useful general introduction to the complex and interesting world of surface activity and surfactant applications.

I want to express my sincere thanks for their support to my family, the publishers, especially Jonathan, Aruna, and Amudhapriya, who put up with a good deal of delay in the completion of the project, and my friends and supporters in ALPHA C.I.S.A. in Río Tercero, Córdoba, Argentina.

Río Tercero, Córdoba
Argentina 2020

Drew Myers

1

An Overview of Surfactant Science and Technology

Continuing rapid changes in our modern, technology-oriented society continues to make it increasingly important for scientists, engineers, regulators, managers, and end users to remain abreast of the latest in the technologies impacting their work. While digital electronics gets the lion's share of the general press, good old-fashioned chemistry remains vitally important for a myriad of manufacturing, processing, and functional operations. Cleaning, lubricating, adhesion, surface release, water repellency, and many more very basic surface and interfacial phenomena remain essential to the proper functioning of the newer technological processes and products.

The scientific and technical journals published worldwide number in the thousands, and this number seems to increase yearly when we consider the electronic journals, prepublication sites, etc. Paralleling the proliferation of scientific literature in general has been an increasing divergence into fields of “pure” science, i.e. studies with their principal goal being a general advancement of basic human knowledge, and “applied” science and technology, in which the research is driven by some anticipated or hoped-for application or solution. Few areas of chemistry have exhibited this growing dichotomy of purpose more than the study of surface and colloid science, especially as applied to surface activity and surface-active materials or surfactants. Even the nomenclature used in discussing materials showing surface activity is varied, depending on the context of the discussion. It is not surprising, then, that the world of surface activity and surface-active agents can, at times, seem complex and confusing to those not intimately involved in it on a day-to-day basis.

When one considers the impact of surface science in general, and emulsions, dispersions, foaming agents, wetting agents, etc., specifically, on our day-to-day existence, the picture that develops reveals the great extent to which these areas of chemistry and chemical technology permeate our lives. From the fundamental aspects of biological membrane formation and function in living cells to the more “far-out” problems related to the behavior of liquids under “unusual” conditions such as high temperature and pressure environments or under low gravity conditions, as for example, how liquids wet the walls of a rocket's fuel tank in a low gravity environment, the physical chemistry of the interactions among various phases at interfaces lies at the root of much of our modern lifestyle.

Industrial concerns, whose very lifeblood may be intimately linked to the application of the basic principles of interfacial interactions, often ignore the potential benefits of fundamental research in these areas in favor of an empirical trial-and-error approach, which may lead to a viable process but one that could possibly be better understood and even significantly improved

by the application of more “fundamental” science. In many cases, the prevailing philosophy seems to be, to paraphrase an adage, “A dollar in the hand is worth two in the laboratory.” Unfortunately, such an approach often results in more dollars down the drain than many management-level decision makers care to admit. Academic researchers, on the other hand, are sometimes guilty of ignoring the potential practical aspects of their work in favor of experimental sophistication and the “Holy Grail” of the definitive theory or model, although the new thinking in academics of “patent everything, just in case” has brought to light some new potential uses of surfactant technology. Neither philosophy alone truly satisfies the needs of our technological existence. Each approach makes its valuable contribution to the overall advancement of human knowledge; however, it sometimes appears that a great deal is lost in the communication gap between the two.

The science and technology of surfactants have possibly suffered a double whammy from the functional divergence of academic and applied research. Academic interest in surfactants, while increasing in recent years, has generally concentrated on highly purified, homogeneous materials, quite often limited to a few compounds such as the classic examples of sodium dodecyl sulfate (SDS) or cetyltrimethylammonium bromide (CTAB) and elegant analytical techniques. While providing a wealth of useful information related to the system under investigation, the application of such information to more complex practical materials and processes is often less than obvious and is sometimes misleading. In the results-oriented industrial environment, with some significant exceptions, surfactant research is often carried out on a “make it work and don’t worry about why!” basis. The industrially interesting materials are usually complex mixtures of homologues and isomers or contain impurities resulting from chemical side reactions, unreacted starting materials, solvents, etc. Particularly significant surface property changes can be induced by the presence of such impurities as inorganic salts or long-chain alcohols or other molecules remaining after processing. While the presence of such impurities and mixtures will often produce superior results in practice, analysis of the process may be difficult because of the unknown or variable nature of the surfactant composition. Considering the limitations imposed by each “school” of surfactant research, it is not surprising to find that a practical fusion of the two approaches can be difficult to achieve.

The different views of surfactant science and technology have spawned their own distinctive terminologies and literatures. While the academic or fundamental investigator may probe the properties of surface-active agents, surfactants, tensides (a very old and seldom used term today), or amphiphiles, the industrial chemist may be concerned with the characteristics of soaps, detergents, emulsifiers, wetting agents, etc. The former group may publish their results primarily in the *Journal of Physical Chemistry*, *Colloids and Surfaces*, *Langmuir*, or the *Journal of Colloid and Interface Science* and the latter in the *Journal of the American Oil Chemists’ Society*, the *Journal of Dispersion Science and Technology*, or one of the other technologically specialized publications aimed at specific areas of application (foods, cosmetics, paints, etc.). All too often, the value of the results to each community can become lost in the sea of manuscripts and the philosophical and operational gulf that sometimes develops between the two.

Before beginning a discussion of specific aspects of the chemistry of surface-active materials and surfactant action, it may be useful to have some idea of the history of surfactants and how their synthesis and use have evolved through the years. Because of parallel developments in various areas of the world, the secrecy of industrial research efforts, and the effects of two world wars, the exact details of the evolution of surfactant science and technology may be subject to some controversy regarding the specific order and timing of specific developments. In any case, the major facts are (hopefully!) correct.

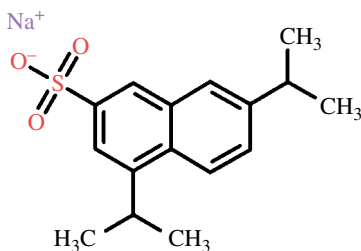
1.1 A Brief History of Surfactant Science and Technology

The pedigree of what are sometimes referred to as “synthetic” surfactants is well documented, unlike that of some of the older “natural” alkali soaps and other plant- or animal-derived materials found to be useful centuries ago by trial and error and that are still used today. However, it is not easy to pinpoint the exact time when the synthetic surfactant industry came into being. In a strictly chemical sense, a soap is a compound formed by the reaction of a fatty acid that is of limited solubility in water with an alkali metal or other organic base to produce a carboxylic acid salt. The resulting salt will exhibit enhanced water solubility sufficient to produce a significant level of surface activity. As a result, soaps were found to have important uses for cleaning purposes. However, those uses can be severely limited by the specific conditions of use, such as temperature, pH, the type and concentration of salts present in their aqueous solutions, etc. Since the traditional soaps are limited in their scope of beneficial surfactant properties for most modern applications, they or newer materials based on petrochemical or other feedstocks require some form of chemical modification to enhance their water solubility and make them more useful in most modern industrial and technological applications. In fact, it is not uncommon to see them referred to as a separate category of materials from other surface-active species as in “soaps and surfactants” or “soaps and detergents.” As already mentioned, it is common today to see some surface-active materials referred to as “natural” and others as being “synthetic” or “chemical” materials. Any such distinction is, of course, a purely artificial distinction since even the traditional soaps require chemical modification to produce useful surface activity and the most synthetic detergents can eventually trace their heritage back to natural sources. Nevertheless, the following discussions will use the natural versus synthetic distinction to “divide the waters,” so to speak. More detailed information on the divide between natural and synthetic surfactants will be given in Chapter 4.

The alkali metal soaps have been used for several thousand years. There is evidence of their use as articles of trade by the Phoenicians as early as 600 BCE. They were also used by the Romans, although it is generally felt that their manufacture was learned from the Celts or some Mediterranean culture. Early soap producers used animal fats and ashes of wood and other plants containing potassium carbonate to produce the neutralized salt. As the mixture of fat, ashes, and water was boiled, the fat was saponified to the free fatty acids, which were subsequently neutralized to the sodium or potassium salts. Other natural surfactants, mostly plant extracts, were used by the Egyptians, among others, for medicinal purposes, embalming, cosmetic formulations, and the like.

The first widely reported non-soap “synthetic” materials employed specifically for their surface-active properties were the sulfated or sulfonated oils. Sulfonated castor oil, also known as “turkey red oil,” was introduced in the late nineteenth century as a dyeing aid and is still used in the textile and leather industries today. The first surfactants for general application that have been traditionally classified as synthetic were developed in Germany during World War I to help overcome shortages of available animal and vegetable fats. Those materials were short-chain alkyl naphthalene sulfonates prepared by the reaction of propyl or butyl alcohols with naphthalene followed by sulfonation. The products, which proved to be only marginally useful as detergents, showed good wetting characteristics and are still in use as such in some industrial applications. They were sold under their original trade name “Nekals,” among others, in Europe and the United States. The chemical processes used for their production were and are rather “messy” in that they do not produce particularly “pure” materials. Rather, the basic products tend to be complex mixtures of isomers including mono-, di-, and trialkyl substitutions. This fact tends to make process control very important to ensure a good degree of reproducibility from batch to batch. The industrial application of alkyl naphthalene sulfates has decreased over the years as they were replaced by more

readily available and more effective alternatives. Nevertheless, they have their uses and are still interesting in a theoretical sense in studies of molecular structure and isomer distribution versus surface activity.



Sodium 4, 7-diisopropyl-2-naphthalenesulfonate

In the late 1920s and early 1930s, the sulfation of long-chain alcohols became common, and the resulting products were sold as the sodium salts. Their general representation is $\text{CH}_3(\text{CH}_2)_n\text{—OSO}_3^- \text{Na}^+$, where $n \geq 11$. Also, in the early 1930s, long-chain alkyl aryl sulfonates with benzene as the aromatic group, represented generally as $\text{CH}_3(\text{CH}_2)_n\text{—C}_6\text{H}_4\text{—SO}_3^- \text{Na}^+$, where $n \geq 8$, appeared in the United States. Both the alcohol sulfates and the alkylbenzene sulfonates (ABS) began to be used as specialized cleaning agents at that time, but they made little impact on the general surfactant or detergent markets. By the end of the World War II, however, the production and use of alkyl aryl sulfonates had almost entirely overwhelmed the alcohol sulfates for use as general cleaning agents, but the alcohol sulfates were beginning to emerge as preferred components in shampoo and other personal care formulations because of their “gentler” characteristics with respect to skin and eye interactions.

In common with other chemical developments during that time, progress in the development of surfactants and detergents was not limited to one family of materials. The explosion of new organic chemical processes and raw materials led to the development of a wide variety of new surface-active compounds and manufacturing processes. The limiting factor in any specific geographical region was almost always the availability of raw materials from which to prepare the desired product. New chemical processing techniques and raw materials also provided access to a greater variety of “natural” products that had a certain esthetic appeal to many people.

Concurrent with the advance of alkyl aryl sulfonates, activities in the United States and Germany led to the development of taurine (2-aminoethane-1-sulfonic acid) derivatives and the alkane sulfates. In the United Kingdom, secondary olefin sulfates derived from petroleum fractions were produced in large quantities. Each of those raw materials had its own special advantages and disadvantages, but in evaluating their feasibility, the producer had to consider such factors as the availability and cost of raw materials, ease of manufacture, the economics of manufacture and distribution, and overall product stability. Because of their ease of manufacture and versatility, the ABS very quickly gained a strong position in the world market for most detergent applications. After World War II, the propylene tetramer (PT), primarily a branched C_9H_{19} alkyl unit, coupled to benzene became a predominant base material. Thus, sulfonated PT-benzenes very rapidly displaced almost all other basic detergents and for the period 1950–1965 constituted more than half of all detergents used throughout the world.

PT-benzenesulfonate held almost undisputed reign as the major ingredient used in washing operations until the early 1960s. Around that time, with the increased use of washing machines and dishwashers in the more industrialized countries, it was noted that sewage effluents were

producing ever greater amounts of foaming in rivers, streams, and lakes throughout the world. In addition, where water was being drawn from wells located close to household discharge points, the water tended to foam when coming out of the tap. Such occurrences were naturally upsetting to many groups and led to investigations into the sources of the foaming agents. The rise of such undesirable phenomena was ultimately attributed to the fact that the PT-benzenesulfonates, generally referred to as alkylbenzene sulfonates, could not be completely degraded by the bacterial and other processes naturally operating in bodies of water, in the soil, and in chemical and physical water treatment plants. It was further determined that it was the branched alkyl (PT) chain that hindered attack by the microorganisms. Fatty acid sulfates, on the other hand, were found to degrade readily, and since all naturally occurring fatty acids from which fatty alcohols are produced are straight chained, it seemed probable that a straight-chain alkylbenzene might prove more easily biodegradable.

Test methods for determining degradability were developed and showed that, in fact, linear alkylbenzene sulfonates (LABS) were significantly more biodegradable and hence ecologically more acceptable than their PT cousins. In most of the industrialized world, detergent producers, voluntarily or by legislation, have switched from PT-benzene to linear alkylbenzene (LAB) units as their basic detergent feedstock.

The change to LAB feedstocks gave some rather surprising results. It was found that detergency in many heavy-duty cleaning formulations using LABS was approximately 10% better than when PT-benzenesulfonates were used. Solutions of the neutralized acid had a lower cloud point, and pastes and slurries had a lower viscosity. The first two results were obviously advantageous, and a lower viscosity in slurries had an advantage when the product was processed into a powder. When the LABS product was to be sold as a liquid or paste detergent, however, the lower viscosity was a detriment to sales appeal and had to be overcome.

Today, even though many of the application areas such as detergents and cleaning products are “mature” industries, the demands of ecology, population growth, fashion, raw material resources, and marketing appeal have caused the technology of surfactants and surfactant application to continue to grow at a healthy rate.

While a large fraction of the business of surfactants is concerned with cleaning operations of one kind or another, the demands of other technological areas have added greatly to their enhanced role in our modern existence. Not only are personal care products becoming an ever greater economic force in terms of dollar value and total volume, but applications as diverse as pharmaceuticals and crude oil recovery are placing more demands on our ability to understand and manipulate interfaces through the action of surface-active agents. As a result, more and more scientists and engineers with little or no knowledge of surface chemistry are being called upon to make use of the unique properties of surfactants. It is with these thoughts in mind that the current project was undertaken.

1.2 Surfactants in the Modern World

The applications of surfactants in science and industry are legion, ranging from primary processes such as the recovery and purification of raw materials in the mining and petroleum industries to enhancing the quality of finished products such as paints, cosmetics, pharmaceuticals, and foods and finally to helping make possible new technologies and new uses for old technologies based on a finer control of interfacial interactions. Figure 1.1 represents a “snapshot” of many of the areas of our lives that are impacted by surface-active materials.

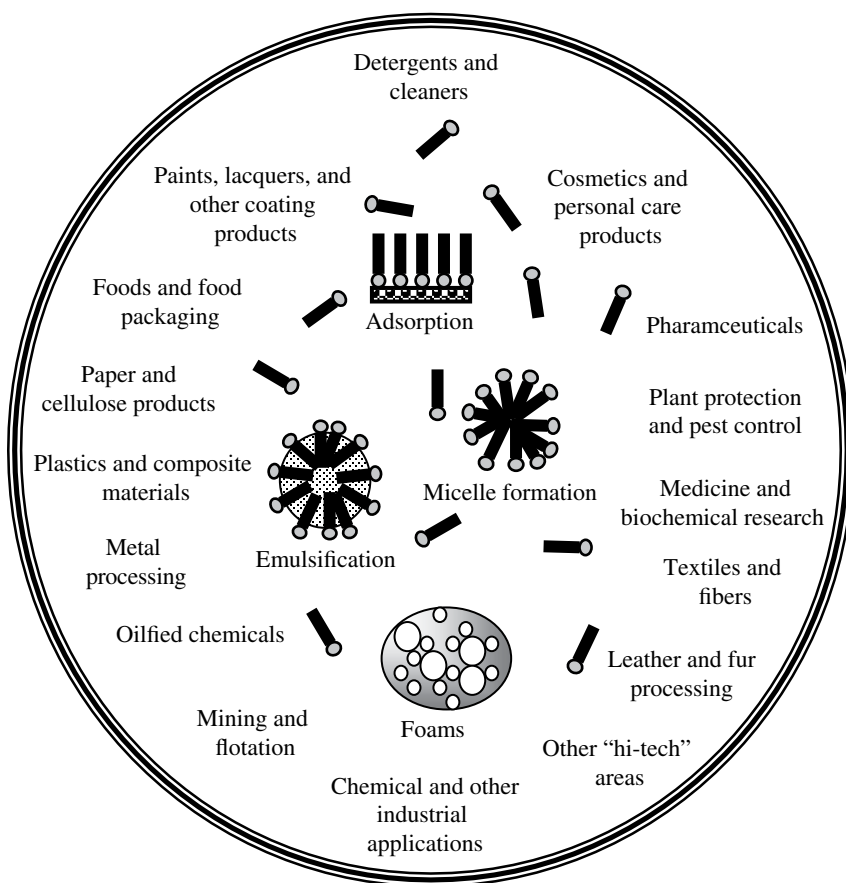


Figure 1.1 Some important, high impact areas of surfactant applications.

Table 1.1 lists just a small sampling of the major areas of surfactant applications currently of vital economic and technological importance in our modern world. A full listing would be very much longer and would likely not include several applications that are not openly discussed for reasons of industrial “secrets,” patent restrictions, and such. As the technological demands placed on product and process additives such as surfactants increase, it seems obvious that our need to understand the relationships between the chemical structures of those materials and their physical manifestations in specific circumstances become much more important.

The properties and applications of surfactants are, as we will see, determined by the molecular balance between two, at least, portions of the surfactant molecule – the lyophobic or hydrophobic (solvent or water hating) and the lyophilic or hydrophilic (solvent or water loving) units making up the complete molecular structure. For many of the applications listed in Table 1.1, the desired properties of the surfactant may vary significantly. For that reason, such characteristics as water or oil solubility, surface tension reducing capability, critical micelle concentration (**cmc**), detergency power, wetting control, and foaming capacity may make a given surfactant perform well in some applications and less well in others. The “universal” surfactant that meets all the varied needs of surfactant applications has yet to emerge from the industrial or academic laboratory and probably never will. Nevertheless, the search will undoubtedly go on, which is good for the science and technology related to surface and interfacial science.

Table 1.1 Some of the major modern applications of surfactants.

Industrial	Consumer goods
Agricultural crop applications	Adhesives
Building materials	Dry cleaning fluids
Cement additives	Foods and beverages
Coal fluidization	Household cleaning and laundering
Coating and leveling additives	Pharmaceuticals
Electroplating	Emulsion polymerization
Photographic products	Soaps, shampoos, creams
Industrial cleaning	Waterproofing
Leather processing	
Lubrication	
Mold release agents	
Ore flotation	
Paper manufacture	
Petroleum recovery	
Surface preparations	
Textiles	
Waterproofing	

Table 1.2 Typical (but not all) characteristics for surfactants that must be evaluated for various applications.

Application	Characteristics
Detergency	Low cmc , good salt and pH stability, biodegradability, desirable foaming properties, eco-friendly, cost
Emulsification	Proper HLB, environmental and biological (safety) for application
Lubrication	Chemical and thermal stability, adsorption at surfaces
Mineral flotation	Proper adsorption characteristics on the ore(s) of interest, low cost
Petroleum recovery	Proper wetting of oil-bearing formations, microemulsion formation and solubilization properties, ease of emulsion breaking after oil recovery, eco-friendly, cost
Pharmaceuticals	Biocompatibility, low toxicity, proper emulsifying properties, cost

The following chapters will provide more details on the structural features that determine the various functional characteristics of surfactants. For now, it suffices to say that each application has specific requirements that will primarily determine the utility of a given surfactant or surfactant combination. Some of the fundamental characteristics that must be evaluated for a surfactant to be evaluated for a specific application are given in Table 1.2. In the applications given in the table and essentially all others, the questions of cost, chemical compatibility, and chemical stability in each use environment will be very important questions.

The fast paced, highly competitive nature of modern industrial developments often demands the fastest, most economical solution to a problem, consistent with the needs of the product. In the realm of surfactant science and technology, it might often be the case that the fastest marginally acceptable solution could be replaced by a superior, possibly more economical, alternative if only the right minds and information could be brought together. Unfortunately, the world of surfactants and surface science historically has not received wide coverage in most academic training situations, and most workers have little familiarity with many of the basic concepts and processes involved. Hopefully, this presentation will help to fill that knowledge gap to a small extent.

1.3 The Economics of Surfactant Science and Technology

The US and world synthetic surfactant industries expanded rapidly in both volume and dollar value following World War II. Before the war, the great majority of cleaning and laundering applications relied for their basic raw materials on fatty acid soaps derived from natural fats and oils such as tallow and coconut oil. During and following the war, the chemical industry developed new and efficient processes to produce petroleum-derived detergent feedstocks based on the PT and benzene. In addition, economic and cultural changes such as increased use of synthetic fibers and automatic washing machines, increased washing frequency, population increases, and, of course, mass marketing through television and other media, all worked to increase the impact of more readily available, at the time, at least, non-fatty-acid-based surfactants. The relative percentages of US surfactant consumption represented by the fatty acid soaps and synthetic detergents changed rapidly during and after the war. In 1945, synthetics represented only about 4% of the total domestic market. By the early 1950s, the fraction had risen to over half of the total, and by the 1970s the soap share had fallen to less than 20%. The declining trend has slowed since then, with the fraction of total worldwide surfactant consumption as soap remaining in the range of 20–22%.

Today, the global growth of the market for synthetic detergents is about 6% in volume per year, although it will obviously vary from one region to another. There is some doubt, however, that this growth rate will continue at a similar pace in the future. Although soaps have continued to decrease as a percentage of the market relative to synthetic detergents, that decline has pretty much leveled off, and the prevalence of that class of products seems to have stabilized. As for detergents, they are increasing with respect to synthetic liquid products and washing powders. Such is not the case for cleaning products and auxiliary products. It is true, however, that the greater part of the market is presently taken by fabric washing and dishwashing products. In several countries, an important market for fabric softeners, which also fall into the surfactant family, has developed in recent years; however, detailed statistical data concerning this market is still not readily available. While the greater part of synthetic detergent consumption has to do with household uses, there are at present many other applications. Products designed for industrial uses are not included in all surfactant market studies. In addition, the use level and surfactant types employed in many industrial products and processes may be closely guarded secrets. Those statistics are therefore not included in most readily available market analyses. Because the soap, cosmetics, and detergent industries market their products directly to the final consumer for the most part, they pay close attention to the demands of the general consumer markets, and, not surprisingly, producers in those product lines, among others, continue to innovate and create new products and product lines that will, they hope, get the attention of their market targets.

Although the surfactant industry continues to place its major emphasis on the synthetic surfactants, demand for the traditional soap products remains relatively strong. In 1987,

approximately 1.5 million metric tons of soaps was used in the three highly industrialized regions of the world – the United States, Western Europe, and Japan. Much higher relative levels of use occur in the less industrialized nations in Africa, Asia, and Latin America, primarily because those areas continue to lack the sophisticated manufacturing capabilities or readily available raw materials for large-scale production of the synthetic precursors to the newer surfactants. In addition, there may be political and social reasons for high levels of soap usage – namely, the ready abundance of natural fats and oils because of significant animal and/or oleochemical industries. Even in the industrialized areas, however, soap demand is substantial.

Because of the nature of the product, its applications, and the availability of the necessary raw materials, soaps will probably maintain a significant market share in the surfactant industry for the foreseeable future. It is generally believed that the demand for surfactants grows in line with the overall gross domestic product (GDP) in a given region, and this is generally what is indicated by production and sales statistics. In developing regions, there is usually a direct link to population growth as well. In the future, it is to be expected that this trend will continue, since surfactants are an important contributor to the quality of life. The European demand for surfactants is relatively steady in terms of volume, in agreement with the overall economic trends in the region; however, social, political, and environmental pressures impose a requirement for more sustainable, effective, and environmentally “friendly” materials, ensuring a continuing demand for innovation and technological development.

Because of their unique physicochemical characteristics and versatility, surfactants have always found ample opportunities to help solve problems in a wide range of modern commercial and industrial applications and perhaps cause a few from time to time. Increasing regulatory constraints and user requirements have led surfactant manufacturers to investigate new and innovative options. The industry continues to be able to find new ways to meet the requirements of growing demands, including surfactants being used to replace traditional solvents, lowering risks, and reducing potential environmental impacts associated with volatile organic solvents. More and more surfactants are playing an important role in the development of new technologies such as nanomaterials, pharmaceutical and microbiological applications, and new oil and gas extraction techniques.

As a general trend, it is widely believed that the demand for surfactants grows more or less at a rate related to the growths of population and GDP, especially in the developing regions of the world. It is expected that such a correlation will continue to be seen in the future since surfactants have become important to the improvement in the quality of life in a very large part of the world's population. Demand in the developed, more “mature” market regions such as the United States, Europe, Japan, and much of Oceania is less dynamic in terms of the volumes of consumption, although the higher levels of regulation in those regions keep pushing the industry to produce more effective, sustainable materials. That, of course, is a good omen for ensuring a continuing push for innovation and new technological development.

As mentioned above, a simple view of statistics suggests that population and GDP growth are the key factors in the growth of the surfactant market. The main growth markets of China, India, South America, and Southeast Asia head the volume growth statistics in agreement with that idea. The correlation is less direct in the growth of mature and technologically and environmentally advanced markets that tend to reflect a higher level of consumer affluence and awareness. Those areas reflect increasing consumption of more specialty surfactants, especially those involving more bio-friendly or “green” materials made using sustainable raw materials. More use of highly formulated laundry products, automatic dishwashers, and specialized cleansing products, together with increased use of personal care products, is seen in the growing “middle class” in regions such as Turkey, Russia, and China. Oil and natural gas production are also major consumers of surfactants, for exploration,

production, and enhanced recovery, leading to increased surfactant consumption in oil-producing regions. The rise of extended oil recovery, including fracking, has driven a large increase in use of surfactants and soluble polymers. More will be said about that in later chapters.

The most important commercial markets for surfactants are household cleaning and personal hygiene, so the growth of those areas will have a substantial impact on overall surfactant market growth. Many people equate the terms “sustainable” and “natural,” sometimes subconsciously and sometimes by media imposition, when, in fact, they are not equivalent. The use of renewable resources often plays a key part in what is seen as sustainability, but the story really is not that simple. The surfactant industry is an important user of renewable resources. Approximately 50% of the mass of all surfactants consumed is coming from renewable resources such as vegetable oils and animal fats, which is substantially better than other mass-consumption chemicals, like plastics and coatings. Renewable carbon sources, however, represent only one piece of the sustainability puzzle with questions of production, distribution, and rational consumption patterns being of equal or greater overall importance.

A key factor in sustainability for the surfactant industry, from a “local” perspective, is for each region to develop the technological and industrial base to provide surfactant “user” industries with products that are produced in the region, thereby reducing environmental burdens associated with transport, controlling the manufacturing conditions, and contributing to wealth production locally.

The surfactant industry has historically obtained its raw materials feedstocks from both renewable biological and petrochemical sources. The wide range of applications and the specific requirements of each application mean that one kind of surfactant chemical composition and structure can never satisfy the demands of client industries and requires the development of surfactants with specific properties for specific applications. While the idea of truly “natural” surfactants is a noble goal, at the present time, there are no fully “natural” products available that have the properties required of most of the surfactants currently used in most industrial and commercial applications, so synthetic chemistry is still essential for providing safe and effective products. There is a good deal of work ongoing in the search for more natural surfactants with good success in many limited areas, but much remains to be done. Some more information in that area is provided in Chapter 4.

Surfactant production consumes significantly less than 1% of oil production as chemical feedstock, while roughly 90% is burned as fuel. A dramatic total switch to renewable materials would place an almost unsupportable burden on global land use by displacing native biological ecosystems with cultivated, nonindigenous plantations as already seen in Southeast Asia, the Amazon basin, and other such areas creating potential ecological disasters. And, of course, there is the fact of creating significant competition with food crops need to feed the booming world population. It is essential for good of coming generations that the use of renewable materials be pursued, but that must be achieved in a truly sustainable way. The creation of “added value” for natural resources can be achieved, but that process can possibly be made more effectively through the more efficient use of a wider range of unconventional biomass, especially that which is produced outside the ecologically delicate tropical regions.

1.4 The Near-Term Economic and Technological Future for Surfactants

The development of new raw materials and advances in synthetic chemical technology have made available new chemical structures that offer an extremely broad menu from which the surfactant shopper can select the materials for a particular need. By carefully analyzing the overall composition

and characteristics of a given system, the investigator or formulator can choose from one of the many available classes of surfactants based on charge type, solubility, adsorption behavior, or any of the other variations related to chemical structure. From the trends in production and use, it is clear that surfactants, although they may seem to constitute a “mature” class of industrial chemicals, have a lot of room for additional growth.

Some classes of surfactants such as the nonionic materials may be especially favored for above-average growth in consumption. Their advantages in performance at lower temperatures, low foaming characteristics, and relative stability at high temperatures and under harsh chemical conditions are definite pluses in many technological applications. Again, a major drawback to the growth of ethoxylated materials may be the nature of the ethylene oxide manufacture, storage, and transport.

Because of their special characteristics, soaps will continue to be important surfactant products. Although increased industrialization in the Third World will undoubtedly lead to greater use of synthetic alternatives, it can be expected that population growth alone will maintain the current levels of soap consumption worldwide. Soaps are the most important single class of surfactants in terms of the generality of their consumption and in terms of their use of renewable raw materials. In terms of raw materials availability, therefore, soaps are very desirable products. As already noted, soaps are especially important in less industrialized countries because the sources are readily renewable and usually locally grown. In addition, the necessary production facilities and technology are relatively simple and inexpensive. In most modern applications, however, soaps are neither efficient nor effective; hence they cannot replace synthetic surfactants. While the use of “natural” soaps has a high emotional rating among environmental groups due to its long tradition of use and “organic” sources, its inferior surfactant characteristics in most industrial and commercial situations require the use of much larger quantities of additives such as phosphates to achieve results approaching those obtained using smaller quantities of synthetic detergents. The net result is a much greater chemical impact on the ecosystem – an important factor in terms of sewage treatment and overall environmental impact, especially in terms of aquatic ecosystems.

While the major surfactant types will continue to dominate the surfactant market for the next decade or more, there will always arise the need for new and improved surfactant products. A few potentially fruitful areas of research include:

- 1) Multifunctional surfactants (e.g. detergent and fabric softener in a single structure).
- 2) More ecologically “acceptable” chemical structures.
- 3) New surfactants based on renewable feedstocks.
- 4) Surfactants with good chemical and thermal stability.
- 5) Natural and highly biocompatible surfactants.
- 6) Polymeric materials that show good surfactant activity and produce viscosity enhancement.

These represent just a few ideas related to surfactant use and possible future growth potential. Some of them will be discussed in more detail in later chapters. For a “mature” industry, surfactants remain an interesting area for research and development.

1.5 Surfactants in the Environment

The use of surfactants throughout the world is increasing at a rate in excess of the population growth because of generally improved living conditions and processed material availability in the less industrially developed Third World countries. Hand in hand with increased surfactant use go

the problems of surfactant disposal. As the more developed nations have learned by painful and expensive experience, the ability of an ecosystem to absorb and degrade waste products such as surfactants can significantly affect the potential usefulness of a given material.

Of particular importance are the effects of surfactants on groundwater and waste treatment operations. Although it could be technologically possible to physically or chemically remove almost all residual surfactants completely from effluent streams, the economic costs would undoubtedly be totally unacceptable. The preferred way to address the problem is to allow nature to take its course and solve the problem by biodegradation mechanisms.

Biodegradation may be defined as the removal or destruction of chemical compounds through the biological action of living organisms. Such degradation may be divided into two stages: (i) primary degradation, leading to modification of the chemical structure of the material sufficient to eliminate any surface-active properties, and (ii) ultimate degradation, in which the material is essentially completely removed from the environment such as carbon dioxide, water, inorganic salts, or other materials that are the normal waste by-products of biological activity. Years of research indicate that it is at the first stage of primary degradation that the chemical structure of a surfactant molecule most heavily impacts biodegradability.

Some of the earliest reports on the biodegradability of synthetic surfactants were made in England, where it was observed that linear secondary alkyl sulfates were biodegradable, while the ABS in use were much more resistant to biological action. It was soon found that the distinction between the linear alkyl sulfates and "ABS" surfactants was not nearly as clear as first suggested. Specifically, it was determined that the biodegradability of a specific ABS sample depended to a large degree on the source, and therefore the chemical structure, of the sample. Early producers of ABS surfactants in England used either petroleum-derived kerosene or tetrapropylene as their basic raw material, without great consideration for the structural differences between the two. As a result, great variability was found in the assay of materials for determination of biodegradability. In fact, the materials derived from tetrapropylene showed little degradation, while the nominally identical materials based on the kerosene feedstocks were much more acceptable. The difference, of course, lay in the degree of branching in the respective alkyl chains.

In 1955 and 1956 it was suggested that the resistance of tetrapropylene-derived ABS surfactants to biodegradation was a result of the highly branched structure of the alkyl group relative to that of the kerosene-derived materials and the linear alkyl sulfates. After extensive research on the best available model surfactant compounds and analogues, it was decided that it was the nature of the hydrophobic group on the surfactant that determined its relative susceptibility to biological action and that the nature and mode of attachment of the hydrophile was of minor significance. Research using an increasingly diverse range of molecular types has continued to support those early conclusions. However, there do exist some questions and concerns about the long-term ecological impact of LABS. Of particular importance are the following:

- 1) LABS are not biodegradable under anaerobic conditions.
- 2) When dissolved LABS enter an aquatic system, what is their effect on adsorption and natural sedimentation phenomena?
- 3) When treated sewage sludge is transferred to the soil, what effects do LABS have on adsorption and soil wetting, and what is its final fate?
- 4) What is the true, ultimate biodegradability of LABS in terms of residues, metabolites, etc.?

Although the chemical basis of surfactant biodegradation continues to be studied in some detail, leading to more specific generalizations concerning the relationship between chemical structure

and biological susceptibility, the following general rules have developed, which seem to cover most surfactant types:

- 1) The chemical structure of the hydrophobic group is the primary factor controlling biodegradability; high degrees of branching, especially at the alkyl terminus, inhibit biodegradation.
- 2) The nature of the hydrophilic group has a minor effect on biodegradability.
- 3) The greater the distance between the hydrophilic group and the terminus of the hydrophobe, the greater the rate of primary degradation.

For a more complete discussion of the complex relationship between the chemical structure of surface-active materials and biodegradability, the interested reader is referred to relevant works listed in the Bibliography.

1.6 A Surfactant Glossary

As indicated above, the world of surfactants and their applications has become one in which the exact meaning of words and phrases is sometimes muddled by the growth of two basic schools of investigators – the industrial scientists and the academicians. To alleviate some of the confusion that may arise on the part of the nonspecialist, I have provided a short list of some of the most common terms encountered in the practice of the art (for in many cases “art” is the best word for it) and science of surface activity and surfactant applications. Although these definitions may differ slightly from those found in other references, they are practical and meaningful for the understanding of the concepts and phenomena under discussion. The list is not, of course, comprehensive, but should cover most of the more common terms one might encounter day to day:

Amphiphilic molecules. Molecules containing contrasting chemical units in terms of the unit’s potential for interaction with polar and nonpolar solvents, usually water and an oil or hydrocarbon phase.

Amphoteric surfactants. Surface-active species that can be either cationic or anionic depending on the pH of the solution, including also those that are zwitterionic (possessing permanent charges of each type).

Anionic surfactants. Surface-active molecules that carry a negative charge on the active portion of the molecule.

Biodegradability. A measure of the ability of a surfactant to be degraded to simpler molecular fragments by the action of biological processes, especially by the bacterial processes present in wastewater treatment plants, the soil, and general surface water systems.

Bolaform surfactants. Surfactants with one or more long hydrophobic chains having a hydrophilic group at the end of each hydrophobic chain or arm.

Cationic surfactants. A surface-active molecule carrying a positive charge on the active portion of the molecule.

Cloud point. Primarily related to nonionic surfactants: the temperature (or temperature range) at which the surfactant begins to lose sufficient water solubility to retain its full extent of surfactant properties and a cloudy dispersion results; the surfactant may also cease to perform some or all normal functions as a surfactant.

Coalescence. The irreversible union or combination of two or more drops (emulsion) or particles (dispersions) to produce a larger unit of lower interfacial area.

Colloid. A system consisting of one substance (the dispersed phase) finely divided and distributed evenly (relatively speaking) throughout a second phase (the dispersion medium or continuous phase).

Contact angle. The angle formed between a solid surface and the tangent to a liquid drop on that surface at the line of contact between the liquid, the solid, and the surrounding phase (usually vapor or air), measured through the liquid.

Counterion. The (generally) non-surface-active portion of an ionic surfactant species necessary for maintaining electrical neutrality.

Critical micelle concentration (cmc). A concentration, or concentration range for mixed surfactants, characteristic of a given surface-active system at which certain solution properties change dramatically, indicating the formation of surfactant aggregates or micelles.

Detergency. The process of removing unwanted material from the surface of a solid by various physicochemical and mechanical means.

Dispersion. The distribution of finely divided solid particles in a liquid phase to produce a system of very high solid–liquid interfacial area.

Dispersion forces. Weak interatomic or intermolecular forces common to all materials; generally attractive for materials in the ground state, although they can have a net repulsive effect in some solid–liquid systems.

Emulsifying agents or emulsifiers. Surfactants or other materials added in small quantities to a mixture of two immiscible liquids for aiding in the formation and stabilization of an emulsion. In the food industry the term may be used for any surfactant species even though its function may have nothing to do with the formation or stabilization of an actual emulsion.

Emulsion. A colloidal suspension of one liquid in another. (A more specific functional definition is given in Chapter 8.)

Fatty acids. A general term for the group of saturated and unsaturated monobasic aliphatic carboxylic acids with hydrocarbon chains of from 6 to 20 carbons. The name derives from the original source of such materials, namely, animal and vegetable fats and oils.

Fatty alcohols. Primary alcohols with carbon numbers in the range of C_6 – C_{20} historically derived from natural fats and oils, but more recently obtainable from petroleum sources.

Flocculation. The (often) reversible aggregation of drops or particles in which interfacial forces allow the close approach or touching of individual units, but the separate identity of each unit is maintained.

Foam booster. An additive that increases the amount or persistence of foam produced by a surfactant system.

Foam inhibitor. An additive designed to retard or prevent the formation of foam in a surfactant solution, usually employed at low concentrations.

Gemini surfactants. Surfactant molecules that have two hydrophobic tails with two hydrophobic head groups attached to each in which the two units are linked by a “spacer” chain between the head groups or along the hydrophobic chain.

Head group (surfactant). A term referring to the portion of a surfactant molecule that imparts solubility to the molecule. Generally used in the context of water solubility.

Hydrogen bonding. Electrostatic interactions between molecules or portions of a molecule resulting from the Lewis acid or base properties of the molecular units. Most commonly applied to water or hydroxyl-containing systems (e.g. alcohols) in the sense of Brønsted–Lowry acid–base theory.

Hydrophile–lipophile balance (HLB). An essentially empirical method for quantifying the surface activity of a species based on its molecular constitution – used primarily in emulsion technology.

Hydrophilic (“water loving”). A descriptive term indicating a tendency on the part of a species to interact strongly with water, sometimes equated (often incorrectly) with “lipophobic,” defined below.

Hydrophobic (“water hating”). The opposite of hydrophilic, having little energetically favorable interaction with water – generally indicating the same characteristics as lipophilic, except that some hydrophobic materials (e.g. perfluoro organics) can also be lipophobic.

Interface. The boundary between two immiscible phases. The phases may be solids, liquids, or vapors, although there cannot be a true interface between two vapor phases. Mathematically, the interface may be described as an infinitely thin line or plane separating the bulk phases at which there will be a sharp transition in properties from those of one phase to those of the other, although in fact it will consist of a region of at least one molecular thickness, but often extending over longer distances.

Interfacial tension. The property of a two-phase system, usually applied to liquid–liquid systems, exhibiting the characteristics of a thin elastic membrane acting along the interface in such a way as to reduce the total interfacial area by an apparent contraction process. Thermodynamically, the interfacial excess free energy resulting from an imbalance of forces acting upon molecules of each phase at or near the interface. (See Surface tension.)

Lipophilic (“fat loving”). A general term used to describe materials that have a high affinity for fatty or organic solvents; essentially the opposite of hydrophilic.

Lipophobic (“fat hating”). The opposite of lipophilic, that is, materials preferring to be in more polar or aqueous media, the major exception being the fluorocarbon materials, which may be both lipophobic and hydrophobic.

London forces. Forces arising from the mutual perturbation of the electron clouds of neighboring atoms or molecules; generally weak (≈ 8 kJ/mol), decreasing approximately as the inverse sixth power of the distance between the interacting units.

Lyophilic (“solvent loving”). A general term applied to a specific solute and solvent system, indicating the solubility relationship between the two. A highly water-soluble material such as acetone would be termed lyophilic in an aqueous context.

Lyophobic (“solvent hating”). The opposite of lyophilic. A hydrocarbon, for example, would be lyophobic in relation to water. If the solvent in question were changed to octane, the hydrocarbon would then become lyophilic.

Micelles. Aggregated units composed of several molecules of a surface-active material, formed because of the thermodynamics of the interactions between the solvent (usually water) and lyophobic (or hydrophobic) portions of the molecule. Micelles may be more or less spherical or take on other geometries, such as rods, disks, etc., depending on the chemical structure of the surfactant molecule and the exact solution composition.

Nonionic surfactants. Surfactants that carry no electrical charge, their water solubility being derived from the presence of polar functionalities capable of significant hydrogen bonding interaction with water (e.g. polyoxyethylene and polyglycidols).

Oleochemicals. Products derived from vegetable oil feedstocks or animal fats.

Self-assembly. The thermodynamically driven process causing amphiphilic molecules to associate spontaneously in solution to form aggregate assembly containing a number of molecules associated through interactions among their hydrophobic tails. The process is usually observed in aqueous solutions, although it does occur to some extent in organic solvent systems.

Soap. The name applied to the alkali salts of natural fatty acids, historically the product of the saponification of natural fats and oils.

Solubilization. The act of making a normally insoluble or minimally material more soluble in a given medium. In the following chapters, the term is applied in two ways: the “solubilization” of a hydrocarbon chain in water by chemical modification – the addition of a head group – and the micellar solubilization of a separate oil phase in water or vice versa.

Spacer chain. A chain of units linking two surfactant-like units to form a double or Gemini surfactant. The spacer can be a methylene chain, usually having between 3 and 12 units, an unsaturated hydrocarbon chain, including aromatic units, or it can contain ether or amine linkages.

Surface-active agent. The descriptive generic term for materials that preferentially adsorb at interfaces because of the presence of both lyophilic and lyophobic structural units, the adsorption generally resulting in the alteration of the surface or interfacial properties of the system.

Surface tension. The property of a liquid evidenced by the apparent presence of a thin elastic membrane along the interface between the liquid and a vapor phase, resulting in a contraction of the interface and reduction of the total interfacial area. Thermodynamically, the surface excess free energy per unit area of interface resulting from an imbalance in the cohesive forces acting on liquid molecules at the surface. The term is most often applied to liquid/vapor interfaces.

Surfactant. The widely employed contraction for “surface-active agents.”

Surfactant tail. In surfactant science, usually used with reference to the hydrophobic portion of the surfactant molecule.

Most of the above terms will be discussed in more detail in later chapters.

2

The Classification of Surfactants

Before we can begin to consider questions related to the whys and wherefores of surfactant structures, it is necessary to have a good idea of exactly what we mean by the term “surface activity” and the phenomena arising from it. In a very general way, leaving mathematics and theory aside for the moment, one can say that surface activity is a thermodynamic free energy-driven process that causes certain types of chemical compounds to preferentially or spontaneously migrate to or locate themselves at boundaries or interfaces between different materials or bulk phases. The general term used for such phenomena is “adsorption.” The process results in the formation of a film, usually but not always a monolayer, at the interface. As pointed out in the Section 1.6, the *adsorption* process is not the same as *absorption*, which indicates the introduction or movement of a material into one or both bulk phases present. Absorption, therefore, is essentially equivalent to the process of “dissolution.” In most cases involving surface activity it is found that both processes may occur, but for this discussion it is the adsorption and/or desorption of the material in question to or from an interface from the continuous phase that is of interest. The bulk phase(s) may be one or all of the possibilities presented by nature.

The preferential or spontaneous adsorption of the material in question results in a net lowering of the free energy of the interface(s) affected. The extent and overall effects of the observed adsorption will depend on various factors including the chemical natures of the phases in contact, the chemical structure of the materials adsorbing at the interface, and the specific interactions of those materials with each phase. In addition to adsorption at interfaces, in situations in which there are no physical interfaces available for the surface active species to adsorb, the non-adsorbed molecules in solution will be thermodynamically driven to lower the total free energy of the system by self-associating in the solution in such a way as to reduce the unfavorable interactions between the molecules and the continuous phase and replace them with favorable interactions among the lyophobic parts of the molecules.

2.1 The Basic Structure of Amphiphilic Molecules

To understand the relationship between the surface activity of a given material and its chemical structure, it is useful to have a handle on the chemistry of the individual molecular components that produce the observed phenomena. The following discussion introduces the basic organic chemical principles involved in common surfactants, ranging from raw materials and sources to the chemical group combinations that result in observed surface activity. The chemical

compositions and synthetic pathways leading to surface-active molecules are primarily limited by the creativity and ingenuity of the synthetic chemist and the production engineer. Therefore, it is impossible to discuss all potential chemical classes of surfactants, their preparations, and subtle variations. However, most surfactants of academic and technological interest can be grouped into a rather limited number of basic chemical types and synthetic processes.

The chemical reactions that produce most commercial surfactants are rather simple, understandable to anyone surviving the first year of organic chemistry. The challenge to the producer lies in the implementation of those reactions on a scale of thousands of kilograms, reproducibly, with high yield and high purity (or at least known levels and types of impurities), and at the lowest cost possible. With very few exceptions, there will always be a necessity to balance the best surfactant activity for an application with the cost of the material that can be borne by the added value of the final product. The challenge to the ultimate user is to understand the chemical, physical, and biological requirements that a candidate material must meet.

Before discussing specific details of surfactant types and possible synthetic pathways, it may be useful to introduce some of the many reactions that can produce surfactant activity in an organic molecule. In that way, the reader can begin to see some of the basic simplicity of surfactant science underlying the imposing mass of structural possibilities.

As a rule, a surface-active molecule or surfactant will be composed of two significantly different chemical groups in terms of their polarity and solubility characteristics. For optimum effectiveness, those two groups will usually be isolated within the molecular structure in a relatively simple way, although some surface-active materials such as polymers, biological materials and other complex systems may not be so easily described. In the “standard” model, the surfactant molecule is usually described as having one portion of the molecule being relatively nonpolar while the other portion is very polar or ionic in character. Since most systems employing surface-active materials are water based or involve water as one of two phases having an interface, the convention is to refer to the nonpolar, or less polar, component as the “tail” and the more polar or ionic component as the “head.” Such molecules are generally referred to as being “amphiphilic.” That basic structure is illustrated in Figure 2.1 for a simple hydrocarbon tail and ionic (salt) head.

The molecular structures having suitable solubility properties for surfactant activity vary with the nature of the solvent system to be employed and the conditions of use. In water, the hydrophobic group (the “tail”) may be, for example, a hydrocarbon, an alkyl aryl group, or a fluorocarbon or siloxane chain of long enough to produce the desired solubility characteristics when bound to a suitable hydrophilic group. As will be shown below, those are just a few examples with more waiting in the wings. The hydrophilic group (the “head”) will be ionic or highly polar, so it can act as a solubilizing functionality in water. In a nonpolar solvent such as hexane, the same groups will function in the opposite sense. As the temperature, pressure, or solvent environment of a surfactant (e.g. cosolvent addition, pH changes, or the addition of electrolytes) varies, significant alterations in the solution and interfacial properties of the system may occur. As a result, modifications in the chemical structure of the surfactant may be needed to maintain a desired degree of



Figure 2.1 The basic molecular structure of a surface-active molecule.

surface activity depending on the exact nature of the continuous phases. It cannot be overemphasized that a given surfactant effect will be intimately tied to the specific solvent system in use. Those variables will be discussed in more detail in later chapters.

2.2 A Systematic Classification of Surfactants

Almost from the beginning of scientific investigations into the synthesis and application of surfactants, a goal of surfactant-related research has been to devise a quantitative way to relate the chemical structure of surface-active molecules directly to their surface and interfacial activity in actual use. The first significant attempt to quantify the relationship between surfactant chemical structures and their activity in a specific application was the “hydrophile–lipophile balance” or HLB, which, by the way, is still found useful today. Described more fully later, the HLB system attempted to relate the molecular composition of a surfactant, as mole percent of hydrophile or “head,” to its surfactant properties. In more recent years, attempts have been made to use the concepts of cohesive energy densities, also called solubility or Hildebrand parameters, to quantify such relationships as surfactant chemical structure, the nature of the solvent, and surfactant activity on a more fundamental atomic and molecular level. Another useful classification scheme is based on the geometry of the surfactant molecules and its effects on the activity of the material. Those and other schemes for predicting surfactant activity based on the specifics of molecular architecture will be addressed in more detail in subsequent chapters.

2.2.1 Surfactant Solubilizing Groups

The solubilizing groups of modern surfactants fall into two general categories: those that ionize in aqueous solution (or highly polar solvents) and those that do not. Obviously, the definition of what part of a molecule is the solubilizing group depends on the solvent system being employed. For example, in water the solubility will be determined by the presence of a highly polar or ionic group, while in organic systems the solubilizing functionality will be the organic portion of the molecule. It is important, therefore, to define the complete system under consideration before discussing surfactant types. As noted before, because the vast majority of surfactant work is concerned with aqueous environments, the terminology employed will generally be that applicable to such systems. Generality will be implied, however.

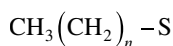
In aqueous systems, by far the most important of surfactant applications in volume and economic impact, the hydrophobic group is generally a long-chain hydrocarbon group, although there are examples using fluorinated or oxygenated hydrocarbon or siloxane chains. The hydrophile or head group will be an ionic or highly polar group that can impart some water solubility to the molecule. The most useful chemical classification of surface-active agents is based on the nature of the hydrophile, with subgroups being based on the nature of the hydrophobe or tail. The four basic classes of surfactants are defined as follows:

- 1) Anionic – The hydrophile is a negatively charged group such as carboxyl ($\text{RCOO}^- \text{M}^+$), sulfonate ($\text{RSO}_3^- \text{M}^+$), sulfate ($\text{ROSO}_3^- \text{M}^+$), or phosphate ($\text{ROPO}_3^- \text{M}^+$).
- 2) Cationic – The hydrophile bears a positive charge, for example, the quaternary ammonium halides ($\text{R}_4\text{N}^+ \text{X}^-$), and the four R-groups may or may not be all the same (they usually are not) but will usually be of the same general family.

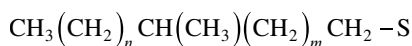
- 3) Nonionic – The hydrophile has no charge but derives its water solubility from highly polar groups such as polyoxyethylene (POE) ($\text{R}-\text{OCH}_2\text{CH}_2\text{O}-$) or R-polyol groups including sugars.
- 4) Amphoteric (and zwitterionic), in which the molecule contains, or can potentially contain, both a negative and a positive charge, such as the sulfobetaines, $\text{RN}^+(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{SO}_3^-$.

In general, the nature of the hydrophobic groups may be significantly more varied than for the hydrophile. Quite often they are long-chain hydrocarbon groups; however, they may include such varied structures as:

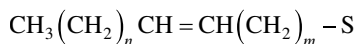
- 1) Long, straight-chain alkyl groups ($n = \text{C}_8-\text{C}_{22}$ with terminal substitution of the head group)



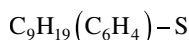
- 2) Branched-chain alkyl groups (C_8-C_{22} , internal substitution)



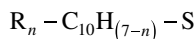
- 3) Unsaturated alkenyl chains such as those derived from vegetable oils



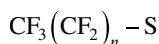
- 4) Alkylbenzenes ($\text{C}_8-\text{C}_{15}\text{C}_6\text{H}_4$ with various substitution patterns)



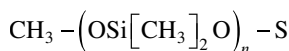
- 5) Alkyl naphthalenes (alkyl R usually C_3 or greater)



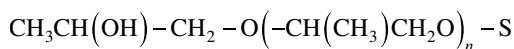
- 6) Fluoroalkyl groups ($n > 4$, partially or completely fluorinated)



- 7) Polydimethylsiloxanes



- 8) Polyoxypropylene glycol derivatives



- 9) Biosurfactants

- 10) Derivatives of natural and synthetic polymers

With such a wide variety of structures available, it is not surprising that the selection of a suitable surfactant for a given application can become a significant problem in terms of making the best choice of material for a given application.

The functionality of ionizing hydrophilic groups derives from their strongly acidic or basic character, which permits the formation of true, highly ionizing salts upon neutralization. In this context, the carboxylic acid group, while not generally considered as such, is classed as a strong acid. The nonionizing, or nonionic hydrophilic groups, on the other hand, have functionalities or element groups that are individually rather weak hydrophiles (alcohols, ethers, esters, etc.) but have an additive effect, so increasing their number in a molecule increases the magnitude of their solubilizing effect.

The simple descriptions of surfactant types given above do not really tell the complete story of surfactant structures. Many surfactants, especially in the food, cosmetics, and personal hygiene industries, for example, have two hydrophobic tails. Those will be discussed in more detail in Chapter 13. Other less well-known classes such as the “Gemini surfactants” and the “bolaform” surfactants or “bolaamphiphiles” are given their own discussion in Chapter 14. By way of introduction, the gemini surfactants have two or more essentially self-contained surfactant “units” linked by a spacer group, and the bolaform surfactants have two head groups linked by one or more long hydrophobic chains. Many “natural” biosurfactants have a number of unusual structures that are difficult to fit into the simple classification schemes. They are discussed in Chapter 4.

2.2.2 Making a Choice

The chemical structure of a surfactant is not the only determining factor in choosing between potential surfactant candidates for a given application. Economic, energetic, ecological, regulatory, and esthetic considerations, in addition to questions of chemical functionality, are becoming more and more important in surfactant structure selection. Since most surfactants are used in formulations that include other ingredients, the relative role of the surfactant must be evaluated along with its physiochemical characteristics.

If the cost of the surfactant is significant compared with that of other components of a system, the least expensive material producing the desired effect will usually be preferred, all other things being equal. Economics, however, cannot be the only factor, since the final performance of the system will be of crucial importance. To make a rational selection of a surfactant, without resorting to an expensive and time-consuming trial-and-error approach, the formulator must have some knowledge of:

- 1) The surface and interfacial phenomena that must be controlled in the specific application.
- 2) The relationships among the structural properties of the available surfactants and their effects on the pertinent interfacial phenomena to be controlled.
- 3) The characteristic chemical and physical properties of the available surfactant choices.
- 4) Any special chemical or biological compatibility requirements of the system.
- 5) Any regulatory limitations on the use a given class of materials (toxicity, allergenic reactions, ecological impact, etc.).
- 6) Public acceptance – “natural” versus “synthetic.”

The following chapters will attempt to provide a basic foundation for making logical surfactant choices – or at least provide a good starting point and grounds for a good “educated guess.”

2.3 The Generic Anatomy of Surfactants

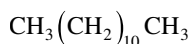
Assuming an “aquocentric” point of view for the moment, surfactants, whether synthetic or of the fatty acid soaps family, are amphiphilic materials that tend to exhibit some solubility in water as well as some affinity for non-aqueous environments – they are nature’s original bipolar chemical

personalities, and we simply would not exist without them. Such an ambivalent character occurs in materials that include two chemically distinct molecular groups or functionalities. For an aqueous system, as already noted, the functionality that would be readily soluble in water is termed the hydrophile; the other functionality, the hydrophobe, would, under normal circumstances, be essentially insoluble in water. It is the “push me, pull you” conflict within the particular molecular structure that produces the unique and amazingly useful family of chemical beasts we know as surfactants.

Chemically speaking, the hydrophilic group is usually, though not always, added synthetically to a hydrophobic material in order to produce a compound with some water solubility. The effectiveness of a given molecular structure as a surfactant will depend critically upon the molecular balance between the hydrophile and the hydrophobe. Attaining the balance necessary to produce the desired result lies at the heart of surfactant science and technology, as does understanding the fundamental chemical principles leading to the observed phenomena. Several empirical schemes have been proposed for quantifying the critical balance between the two parts of surfactant molecules and relating that balance to the activity of the material in a given application. Some of those ideas will be covered in more detail in later chapters. For now, we will see what some relatively minor structural changes can do to the character of the simple hydrocarbon molecule, *n*-dodecane.

2.3.1 The Many Faces of Dodecane

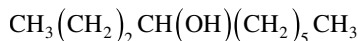
As the root of our surfactant family tree, we will consider the compound *n*-dodecane



This material is a hydrocarbon with essentially no solubility in water and is just about as hydrophobic as one could want, in a practical sense. The hydrocarbon chain is, by nature, somewhat unreactive chemically. In order to modify the molecule, it is necessary to open a “door” that will give chemical access to more of the tools of the synthetic trade. If one of the terminal hydrogen atoms on the chain is exchanged for an —OH group, for example, the new material, 1-dodecanol, still has relatively low solubility in water, but it increases substantially relative to the parent hydrocarbon:



While such a modification seems pretty simple on paper, the actual process can be pretty messy, involving a rather random process of halogenation followed by substitution to form the alcohol. For purposes of the current discussion, however, we will pretend to live in a simpler world and assume that only the desired product is produced. If the alcohol functionality is placed internally on the hydrocarbon chain, as in 3-dodecanol, the resulting material will be similar to the primary alcohol but will have slightly different solubility characteristics:

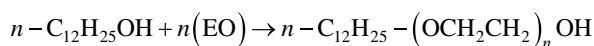


Solubility differences among chemical isomers will generally be evident in other functional modifications. They may also be evident in changes in chemical reactivity and substitution patterns in subsequent chemical reactions. The effects of the position of substitution on surfactant properties can be quite significant and will be discussed in more detail later. Once formed, the

alcohol can be sulfated to produce the dodecane sulfuric acid ester, a strongly acidic compound with good water solubility. When the sulfuric acid ester is neutralized with alkali, certain alkaline earth metals, or organic amines, the material becomes highly soluble in water and is an excellent surfactant. It is, in fact, probably the most extensively studied and best understood surfactant known to science – sodium dodecyl sulfate or SDS:



If the original *n*-dodecanol is treated with ethylene oxide (EO) and base catalyst, the material obtained is a dodecyl POE polyether:



Such molecules can have widely varying solubility characteristics, depending on the value of *n*, the number of EO groups added to the molecule. Because of the nature of the reaction, the value of *n* will always be an average with a relatively large distribution of values. If *n* = 10, the material will be soluble in water and will show good surfactant properties. If *n* is as little as 5, its water solubility will decrease significantly, as will its usefulness as a surfactant. If *n* is taken to 20 or higher, high water solubility is attained, but most of the good surfactant qualities will be lost. For *n* less than 5, the material will have little significant water solubility.

If the original *n*-dodecanol is oxidized to dodecanoic acid the resultant acid has very limited water solubility; however, when neutralized with alkali it becomes water soluble, a classic soap. Although in this example the dodecanoic acid is hypothetically derived from a petroleum source, it will be chemically indistinguishable from the same molecule derived from a “natural” source such as vegetable oils or animal fats. It is a “fatty acid,” its original source notwithstanding:



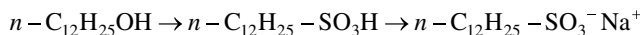
The alkali carboxylate will be a reasonably good surfactant for many applications, but if the hydrocarbon chain length were increased to 16 or 18 carbons, many of the surfactant properties would be even better, illustrating the importance of obtaining the proper balance between the hydrophilic and hydrophobic portions of the molecule. It should be pointed out that long, straight-chain carboxylic acids used in surfactant manufacture such as dodecanoic acid are not synthetic. They are amply abundant derived from vegetable and animal fats and oils.

A major drawback to the use of the classic alkali soaps has always been their great sensitivity to their aqueous environment. They are often poorly soluble in cold water and are always sensitive to the presence of polyvalent metal ions in solution. The main components of so-called hard water are calcium, magnesium, and other divalent and trivalent cations. In the presence of such materials, the carboxylate soaps form salts of low water solubility that precipitate to produce scummy deposits, commonly encountered as the “bathtub ring.” Their solubility in water is simply too low for the system to attain a high enough concentration to produce useful results. In nonaqueous solvents, on the other hand, the polyvalent salts of carboxylate soaps exhibit significantly enhanced solubility and perform admirably in many surfactant functions.

Carboxylate soaps are also strongly affected by changes in solution pH and temperature. Their solubility in water increases significantly with increases in temperature, as does their usefulness as cleaners, the reverse obviously being the case. The sensitivity of the carboxylate soaps to the presence of commonly encountered ions, their sensitivity to pH changes, and their decreased solubility

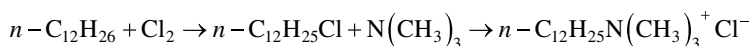
in cold water were the driving forces for the development of synthetic surfactants that would not be so adversely affected by the common circumstances of hard water and cool washing temperatures.

Continuing with the example of dodecane-based surfactant materials, the parent hydrocarbon can be sulfated to yield dodecane sulfonic acid, which closely resembles the sulfuric acid ester discussed previously and has similar water solubility:



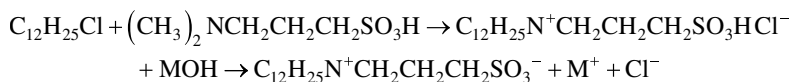
When neutralized with the proper base, the resulting material is an excellent surfactant. It should be noted that while the sulfonic acid is chemically related to the ester, their solution and surfactant properties are not identical, so their potential applications may be different as well. The hydrocarbon sulfonates are generally more chemically stable than the sulfate esters, but the economics of their preparation is an impediment to their widespread use.

If the original dodecane molecule were terminally chlorinated and reacted with trimethylamine, the resulting compound would be dodecyl trimethylammonium chloride, a water-soluble compound exhibiting some surfactant properties, but not generally as useful as the anionic analogues:



The utility of such compounds is limited not so much by their surface activity as by their interaction with various oppositely charged components found in practical systems.

To this point three of the four general classes of surfactants so far defined – anionic, nonionic, and cationic – have been covered. To produce an example of the fourth class, an amphoteric or zwitterionic surfactant, it is only necessary to react the dodecyl chloride prepared above with a difunctional material such as *N,N*-dimethyl-3-aminopropane-1-sulfonic acid:



The result is just one of several possible chemical types that possess the amphoteric or zwitterionic character of this class of materials. Under acidic conditions, the molecule carries a net positive charge. Under basic conditions, the acid is neutralized, and the molecule carries both a positive and negative charge. In this context, we are talking about the electrical nature of the surface-active portion of the molecule and not any associated, but non-surface-active ions such as Cl^- or M^+ .

The number of chemical modifications of the dodecane or similar simple hydrocarbon molecules that can lead to materials with good surfactant characteristics is impressive. When hydrocarbons containing aromatic groups, unsaturation, branching, heteroatom substitution, polymers, or other interesting functionalities are considered, the synthetic possibilities seem almost unlimited. Only imagination, time, and money seem to limit our indulgence in creative molecular architecture.

In each example discussed above, an aqueous “solubilizing group” has been added to the basic hydrophobe to produce materials with varying amounts of useful surfactant characteristics. When one considers the wide variety of hydrophobic groups that can be coupled with the relatively

simple hydrophiles so far discussed and add in more complex and novel structures, the number of combinations becomes impressive. When viewed in that light, the existence of thousands of distinct surfactant structures does not seem surprising.

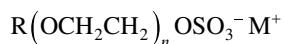
Using the evolution of dodecane-based surfactant structures as a jumping-off point, the discussion will now turn to more specific examples of surfactant building blocks. As noted, the chemical possibilities for surfactant synthesis seem almost limitless. The following discussions, on the other hand, will be limited by space and time and are designed as guides rather than a comprehensive compilation.

2.3.2 Surfactant Solubilizing Groups

As already mentioned, the solubilizing groups of modern surfactants fall into two general categories: those that ionize in aqueous solution (or highly polar solvents) and those that do not. Obviously, the definition of what part of a molecule is the solubilizing group depends on the solvent system being employed. For example, in water the solubility will be determined by the presence of a highly polar or ionic group, while in organic systems the solubilizing functionality will be the organic portion of the molecule. It is important, therefore, to define the complete system under consideration before discussing surfactant types. As noted before, because the majority of surfactant work is concerned with aqueous environments, the terminology employed will generally be that applicable to such systems. Generality will be implied, however.

The functionality of ionizing hydrophiles derives from a strongly acidic or basic character, which leads to the formation of highly ionizing salts on neutralization with appropriate bases or acids. In this context, the carboxylic acid group, while not generally considered as such in acid–base theory, is classified as a strong acid. The nonionizing or nonionic hydrophilic groups, on the other hand, have functionalities or groups that are individually rather weak hydrophiles (alcohols, ethers, esters, etc.) but have an additive effect, so increasing their number in a molecule increases the magnitude of their solubilizing effect.

The most common hydrophilic groups encountered in surfactants today are illustrated in Table 2.1, where, as already noted, R designates some suitable hydrophobic group that imparts surface activity, M^+ is an inorganic or organic cation, and X^- is an anion (halide, acetate, etc.). The list is in no way complete, but the great majority of surfactants available commercially fall into one of those classes. It is possible, and sometimes even advantageous, to combine two or more of the functionalities above to produce materials with properties superior to a monofunctional material. Prime examples would be the alcohol ether sulfates in which a POE nonionic material is terminally sulfated



and, of course, the zwitterionic and amphoteric materials noted, which often exhibit the advantages of both ionic and nonionic surfactants while having fewer of their potential drawbacks. The “hybrid” classes of surfactants, while not yet composing a major fraction of total surfactant consumption, can be particularly useful because of their flexibility and, especially in personal care items such as shampoos, because of the low level of eye and skin irritation they are often found to produce. Building on the basic hydrophilic functionalities discussed above, we now turn our attention to some of the specific structural subgroups derived from the more common hydrophobic groups.

Table 2.1 The most commonly encountered hydrophilic groups in commercially available surfactants.

General class name	Generalized solubilizing structure
<i>Anionic</i>	
Sulfonates	$R-SO_3^- M^+$
Sulfates	$R-OSO_3^- M^+$
Polyoxyethylene sulfates	$R-OCH_2CH_2(OCH_2CH_2)_nOSO_3^- M^+$
Carboxylates	$R-COO^- M^+$
Phosphates	$R-OPO_3^- M^+$
<i>Cationic</i>	
Ammonium	$R-N^+R'_xH_yX^- (x = 1-3, y = 3-1)$
Quaternary ammonium	$R-N^+R'_3X^-$
<i>Nonionic</i>	
Polyoxyethylene (POE)	$R-OCH_2CH_2(OCH_2CH_2)_nOH$
Polyols	$R-O(CH_2-CH(OH))_n-CH_2CH_2OH$
Sucrose esters	$R-O-C_6H_7O(OH)_3-O-C_6H_7(OH)_4$
Polyglycidyl esters	$R-(OCH_2CH[CH_2OH]CH_2)_n- \dots -OCH_2CH[CH_2OH]CH_2OH$
<i>Amphoteric or zwitterionic</i>	
Betaines	$R-N^+(CH_3)_2CH_2COO^-$
Sulfobetaines	$R-N^+(CH_3)_2CH_2CH_2SO_3^-$
Amine oxides	$R-N^+(R')_2-O^-$

2.3.3 Common Surfactant Hydrophobic Groups

By far the most common hydrophobic group used in surfactants is the hydrocarbon radical having a range of 8–22 carbon atoms. Commercially there are two main sources for such materials that are both inexpensive (relatively speaking) and available in sufficient quantity to be economically feasible: “natural” or biological sources such as agriculture and the petroleum industry (which is, of course, ultimately biological). Figure 2.2 indicates some evolutionary pathways from raw materials to final surfactant product. There are, of course, alternative routes to the same materials, as well as other surfactant types that require more elaborate synthetic schemes. Those shown, however, constitute the bulk of the synthetic materials used today.

Many, if not most, surfactant starting materials are not chemically pure materials. In fact, for economic and technical reasons, most surfactant feedstocks are mixtures of isomers with their designation reflecting some average value of the hydrocarbon chain length included rather than reflecting a “true” chemical composition. In some cases, isomeric composition may be indicated in the surfactant name or description, while in others the user is left somewhat in the dark. The name “sodium dodecyl sulfate,” for example, implies a composition containing only C_{12} carbon chains. The material referred to as “sodium lauryl sulfate,” on the other hand, is nominally a C_{12} surfactant but will contain some longer- and shorter-chain homologues. Each source of raw materials may have its own local geographic or economic advantage, so that nominally identical surfactants may exhibit slight differences in surfactant activity due to the subtle influences of raw materials variations. Such considerations may not be important for most applications but should be kept in mind in critical situations.

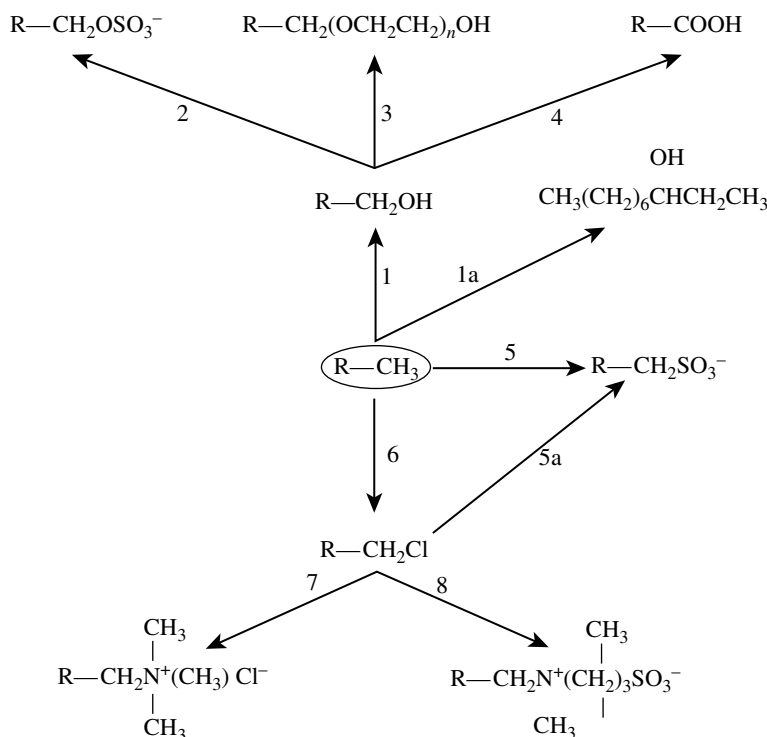


Figure 2.2 Evolutionary pathways for some of the more important types of commercial surfactants.

2.3.3.1 The Natural Fatty Acids

One of the major sources of raw materials for the commercial production of surfactants is also the oldest source – agriculture. Fats and oils (oleochemicals), products of nature’s ingenuity and man’s labor, are triglyceride esters of fatty acids, which can be readily hydrolyzed to the free fatty acids and glycerol. Naturally occurring plant or animal fatty acids usually contains an even number of carbon atoms arranged in a straight chain (no branching), so groups symbolized by an R in abbreviated nomenclature will contain an odd number that is one less than the corresponding acid. The carbons are linked together in a straight chain with a wide range of chain lengths, those with 16 and 18 carbons being the most common. The chains may be saturated, in which case the R group has the formula C_nH_{2n+1} , or they may have one or more double bonds along the chain. Hydroxyl groups along the chain are uncommon, but not unknown, especially in soaps made using castor oil (ricinoleic acid). Other substitutions are rare.

Commercially, the largest surfactant outlet for fatty acids is conversion to soap by neutralization with alkali. In a strict sense, this may be considered to be a synthetic process, and soap therefore a synthetic surfactant. However, common usage reserves the term “synthetic” for the more modern products of chemical technology, primarily petroleum derived, that have been developed in the twentieth century and generally show important improvements over the older soap technology. The chemical processes required for the production of modern surfactants and detergents are also usually much more complicated than the simple neutralization involved in soap manufacture. In this context, the term “simple” is relative, as is well known to anyone who has ever tried to make homemade soap.

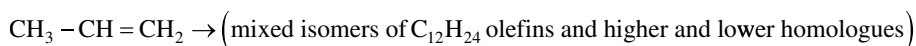
2.3.3.2 Saturated Hydrocarbons or Paraffins

The hydrophobic groups derived from petroleum are principally hydrocarbons, coming originally from the paraffinic or higher boiling fractions of crude oil distillates. The chain lengths most suitable for surfactant hydrophobes, C_{10} – C_{20} , occur in the crude oil cuts boiling somewhat higher than gasoline, namely, kerosene and above. The main components of kerosene are saturated hydrocarbons ranging from $C_{10}H_{22}$ to $C_{15}H_{32}$, ordinarily containing 10–25% of straight-chain homologues. There may be significant amounts of branched-chain isomers present, in addition to quantities of saturated cyclic derivatives, alkyl benzenes, naphthalenes, and minor amounts of other polycyclic aromatics.

The paraffins have the disadvantage of being relatively chemically unreactive, so direct conversion to surfactants is difficult. As discussed above, substitution of one or more hydrogen atoms with halogen offers a pathway to some surfactant systems, but manufacturing complications can be an impediment. It is usually necessary to synthesize the surfactant by way of some more reactive intermediate structures, commonly olefins, alkyl benzenes, or alcohols. Such compounds contain reactive sites that are more easily linked to the required solubilizing groups.

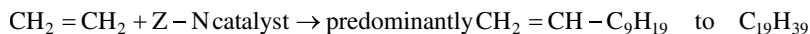
2.3.3.3 Olefins

Olefins with the desired chain length are prepared by building up molecules from smaller olefins (oligomerization), by breaking down (cracking) larger molecules or by direct chemical modification of paraffins of the desired chain length. An important historic example of surfactant-grade olefin production by the oligomerization process is the preparation of tetrapropylene, $C_{12}H_{24}$:



This may be prepared by the oligomerization of propylene, a by-product of refinery operations, under the influence of a phosphoric acid catalyst. The reaction conditions are drastic, and extensive random reorganization of the product molecules occurs with substantial formation of intermediate isomers in the C_{10} – C_{14} range. The final product is composed of a variety of highly branched isomers and homologues, with the double bond usually situated internally in the molecule.

A second type of built-up olefin is that obtained by the polymerization of ethylene using a Ziegler–Natta catalyst. Such materials are predominantly linear with even carbon numbers, although branched isomers are present in small amounts. The ethylene raw material historically has been more expensive than propylene. The catalyst is also more expensive, and the reaction conditions are more sensitive and critical than those for propylene oligomerization:



Production of surfactant or detergent-class olefins from higher molecular weight precursors is accomplished by the cracking process, which uses high temperatures to split high molecular weight paraffins into smaller units. A catalyst may also be employed in the process. Basically, the reaction involves the splitting of a paraffin into two smaller molecules, a paraffin and an olefin. In practice, a wide range of products is obtained because the original molecules may split at any spot along the chain and the resulting products may themselves be cracked further. Each olefin molecule that undergoes such secondary cracking produces two more olefins, so the paraffin content becomes progressively smaller. The olefins produced are predominantly α -olefins, with the double bond located at the terminus of the molecule, as indicated above. If the original cracking stock is linear, the product olefins will be predominantly linear; if branched or cyclic structures were originally present, such structures will also appear in the product.

A third route to detergent olefins is from paraffins of the same chain length. In principle, it is necessary only to remove two hydrogen atoms from an adjacent pair of carbons along the chain to produce the desired olefin, but the difficulties of dehydrogenation are such that a two-step process of chlorination and dehydrochlorination has been developed. In either process the reaction easily proceeds past the desired stage to give polychlorinated paraffins and polyolefins, all undesirable by-products.

2.3.3.4 Alkyl Benzenes

Alkyl benzenes first made their appearance as hydrophobic groups in the late 1940s as a result of new industrial processing capabilities related to the chemistry and chemical engineering of aromatic alkylation reactions. They were prepared by the more or less random chlorination of kerosene and the subsequent Friedel–Crafts alkylation of benzene. Their real dominance in the field began in the early 1950s with the appearance of tetrapropylene-based alkyl benzenes, a functionally better and cheaper product obtained in a one-step process involving addition of benzene across the double bond of the olefin. A variety of Friedel–Crafts catalysts may be employed including aluminum chloride or hydrogen fluoride.

The alkyl group of the alkyl benzene might be expected to have a carbon backbone identical to that of the olefin from which it was derived. This is true in most, but not all, cases because the alkylation process may cause rearrangement of the carbons in the chain. Furthermore, the reaction of the benzene ring with the double bond of the olefin involves a number of intermediate steps during which isomerization may occur, so the benzene may finally link on at some position other than that of the original double bond. Thus, each of the many species that make up the olefin feedstock may give rise to several isomeric alkyl benzenes, and the resulting material will be an even more complex mixture than the original. Gas chromatographic analysis of typical products may show more than 100 at least partially resolved components.

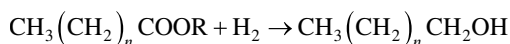
Propylene-derived alkyl benzenes were pretty much phased out in the 1960s because of their exceptional (and undesirable) biological stability and were replaced by the linear alkyl benzenes prepared from linear olefins or intermediate chlorinated paraffins. These products, like the fully saturated tetrapropylene products, have a chain length that may range from C_8 through C_{16} , variously distributed according to the specific preparation procedure and the properties desired in the final surfactant. The nominal carbon values for most commercial products are C_8 and C_9 alkyl groups.

The alkylation of benzene with a linear olefin commonly results in a mixture of all possible linear secondary alkyl benzenes with that total carbon number, even though the original olefin may have been a pure compound. During the alkylation reaction a rearrangement occurs so that the ring bonds at any of the carbon atoms along the chain except the ends. Primary alkyl benzenes are not formed in this process. At equilibrium, the same isomers will be formed regardless of the original location of the double bond. Indeed, any of the five dodecylbenzene isomers can be converted into a mixture of all five by treatment with $AlCl_3$, the catalyst often used in the alkylation. A similar mixture is obtained using the chloroparaffin process. Since there is not much difference in the reactivity of the 26 hydrogen atoms in dodecane, all possible monochloro-isomers are present in the chlorododecane, and all possible phenyl isomers are present in the resulting dodecylbenzene mixture, including a small amount of the primary isomer.

2.3.3.5 Alcohols

Long-chain alcohols have been used as a source of surfactant hydrophobes since the earliest days of synthetic detergent manufacture. Linear alcohols have been used since the beginning, branched alcohols being a more recent addition to the chemical arsenal.

The classical route to a linear alcohol is by the reduction of the carboxyl group of a fatty acid. Actually, an ester of the carboxylic acid is usually employed, since the carboxyl group itself reacts rather sluggishly. Lauryl and tallow alcohols are two of the most commonly used substrates for surfactant synthesis. The first is not only derived from lauric acid, predominantly a C₁₂ acid, but also usually containing some amounts of lower and higher homologues. The tallow alcohols average around C₁₈. Partially or completely hydrogenated fatty acids from oil seeds usually have carbon chains in the C₁₆–C₁₈ range. Depending on the reduction process used, they may contain some unsaturated alcohols derived from the unsaturated acids in the original fatty acids:



Since the early 1960s linear primary alcohols have been available from petroleum sources, namely, ethylene. The process for their preparation is similar to the Ziegler process for linear olefins, except that the last step is an oxidative one yielding the alcohol directly instead of an olefin. As oligomers of ethylene, the Ziegler-derived alcohols are produced in even-numbered chain lengths. The average chain length and distribution of homologues can be controlled somewhat by the reaction conditions and completely by subsequent distillation. The —OH groups are at the end of the chain (terminal), so they are identical to the alcohols derived from the natural fatty acids. However, the two products may differ slightly because the amounts and distribution of minor products and impurities.

Branched-chain alcohols were used extensively for surfactant manufacture prior to the changeover to the more readily biodegradable linear products. They were usually derived from polypropylenes by the “oxo” process, which involves catalytic addition of carbon monoxide and hydrogen to the double bond in a sequence of reactions. Therefore, the tetrapropylene derivative is nominally a C₁₃ alcohol, as highly branched as the original raw material.

If a linear α -olefin is used in the oxo process, addition may occur at either end of the double bond to give a mixture of linear primary and methyl-branched secondary alcohols. Substitution further down the chain occurs only in small amounts, and with the proper choice of reaction conditions, the proportion of linear primary alcohol may reach 80% or more.

The development of linear paraffin feedstocks for the production of linear alkyl sulfates (LAS) also made many secondary alcohols feasible as surfactant hydrophobes. Here the —OH group may be introduced by reaction of the paraffin with oxygen or by chlorination and subsequent hydrolysis. In either case all possible isomers are formed, and the OH group is found on any of the carbons along the chain.

2.3.3.6 Alkyl Phenols

The alkyl phenol hydrophobes are produced by addition of phenol to the double bond of an olefin. The alkyl group may be linked to the ring either ortho-, meta-, or para- to the hydroxyl group, and the position can have a significant impact on the characteristics of the resulting surfactant. The earlier commercial products were derived from branched olefins such as octyl phenols from isobutylene and nonylphenols from tripropylene. More recently, linear alkylphenols have become available with the development of linear olefins for LAS.

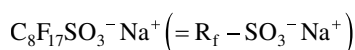
2.3.3.7 Polyoxypropylenes

The polyoxypropylene, oligomers of propylene oxide, can be cited as an example of non-hydrocarbon hydrophobes. A complete line of surfactants known commercially as the “Pluronics” have been developed commercially. These are block copolymers of propylene

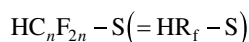
oxide and ethylene oxide. By careful control of the relative amounts of each component incorporated into the polymer, it is possible to exercise a subtle control over the solubility and surfactant character of the product. The character of other hydrophobes such as alcohols and alkyl phenols may also be modified by addition of propylene oxide.

2.3.3.8 Fluorocarbons

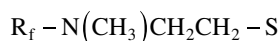
An important modern addition to the spectrum of available hydrophobic functionalities for the design of surfactants is that in which fluorine is substituted for hydrogen on the carbon chain. Substitution may be complete to produce the “perfluoro” materials (R_f) such as sodium heptadecafluorooctane sulfonate:



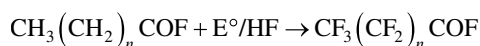
or they may possess a terminal hydrogen (HR_f) with the general structure



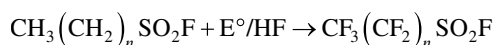
where S may be any of the solubilizing groups discussed. Hydrocarbon groups may also be encountered associated with linking functionalities such as



The most commonly encountered commercial fluorosurfactants are prepared by the electrolytic fluorination of the corresponding alkyl carboxylic acid fluoride or sulfonyl fluoride:



or

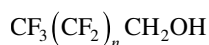


The fluorinated products may then be hydrolyzed to the corresponding acid and neutralized or functionalized by reaction of the reactive acid fluoride to introduce linking groups such as the sodium 2-sulfonamidoethane sulfonate:



Although normal straight-chain hydrocarbon starting materials may be used in the electrolytic process, some branching will always result, commonly yielding materials with up to 30% branched isomers.

Perfluorinated alcohols cannot be prepared directly from the electrolytic process since they require the reduction of the corresponding carboxylic acid to yield structures such as



The presence of the two hydrogens alpha to the hydroxyl is synthetically useful; however, because the perfluorinated alcohols cannot be effectively used in esterification reactions, the perfluorinated products, when obtained at all, are very unstable to hydrolysis.

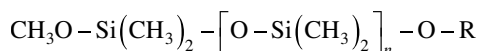
Hydrogen-terminated materials can be produced by the oligomerization of tetrafluoroethylene. In such a reaction, the product will be a mixture of homologous alcohols with an average molecular

weight similar to those obtained in the preparation of POE-containing materials. It is also possible to obtain perfluorinated materials in the oligomerization process.

As a class, fluorocarbon compounds in which all carbon–hydrogen bonds have been replaced by carbon–fluorine possess the lowest surface tensions and surface energies of any substances currently known to science. If surface activity is defined as the tendency of a substance to reduce the total free energy of a system by preferential adsorption at available surfaces and interfaces, or aggregation to form micelles, the fluorocarbon surfactants can also be considered to be the most surface-active materials around. In addition, the electronic nature of the carbon–fluorine bond is such as to make them the most chemically stable of surfactants, able to withstand temperatures and chemical environments that would quickly destroy conventional hydrocarbon-based materials. As a result of those characteristics, the fluorocarbons have found applications in many technological areas in which hydrocarbons are either much less effective or chemically incompatible. The different chemical and electrical properties of the fluorine atom relative to hydrogen have also resulted in fluorinated surfactants finding applications for the modification of the surface properties of coated materials, especially with respect to triboelectric charging phenomena. Unfortunately, the wide use of fluorocarbon surfactants is limited by their relatively high cost, their environmental persistence, and the persistence and possible detrimental health effects of intermediates in their production. In some situations, however, their superior surface activity is essential and outweighs other factors.

2.3.3.9 Silicone Surfactants

Another type of non-hydrocarbon-based hydrophobic group gaining importance in the field of surfactant technology is that in which siloxane oligomers are functionalized to produce water-soluble materials:



The resulting materials usually exhibit surface activities falling somewhere between those of the normal hydrocarbons and the fluorinated compounds just discussed. Because of the nature of the siloxane linkage, such surfactants do not always follow the usual rules of surfactant activity with regard to such phenomena as micelle formation and solubilization. They are very effective at the liquid–air interface, even in many nonaqueous solvents, and find wide application as antifoaming agents (see Chapter 8). A great deal of technical information on siloxane-based surfactants is not available in the open literature, possibly because of difficulties faced in characterizing the siloxane group and because much of the work in the area is of a proprietary nature.

2.3.3.10 Miscellaneous Biological Structures

In more modern developments, a great deal of new research is now going on related to surfactants and amphiphilic materials produced by fermentations and other biological processes. As might be expected based on “normal” natural products chemistry, biologically produced amphiphiles are usually more complex molecules including amino acid or proteins functionalities, lipids, sugars, and all of the other twists and turns that nature has devised throughout evolution. In fact, it is found that the exact structure of the amphiphile produced by a given organism will vary according to the conditions of the fermentation and the exact nature of the “food” provided to the relevant organism. More will be said about biological surfactant systems in Chapter 4.

When properly combined, the major chemical components of surfactants produce the various classes of amphiphilic materials introduced above. The discussion will now turn to a more detailed

description of each of the four primary classes with regard to their preparation and some general applications. While the coverage is not comprehensive, it does illustrate the major points of interest applicable to each class. With all of the possible chemical structures available for surfactant synthesis, it is necessary to have some logical system of classification to guide the user to the material best suited to immediate and future needs.

2.4 The Systematic Classification of Surfactants

Surfactants may be classified in several ways, depending on the needs and intentions of the people involved. One of the more common schemes relies on classification by application. Surfactants may be classified as emulsifiers, foaming agents, wetting agents, dispersants, etc. For the user whose work is confined to one type of application, such a classification scheme has certain obvious advantages. It does not, however, tell much about the specific chemical nature of the surfactant itself, nor does it give much guidance as to other possible uses of a given material.

Surfactants may also be generally classified according to some physical characteristic such as primarily water or oil solubility or stability in harsh environments. Alternatively, some specific aspect of the chemical structure of the materials in question may serve as the primary basis for classification, an example being the type of linking group between the hydrophile and the hydrophobe (e.g. oxygen, nitrogen, amide, sulfonamide, etc.). Perhaps the most useful scheme from a general point of view, however, is that based upon the overall chemical structure of the materials in question. In such a classification system, it is possible to more easily correlate chemical structures with interfacial activity and thereby develop some general rules of surfactant structure–performance relationships.

As already mentioned, the simplest classification procedure is that in which the primary type is determined by the nature of the solubilizing functionality. Within each primary classification by solubilizing group, there will exist subgroups according to the nature of the lyophobic group. It is possible to construct a classification system as complex as one might like, breaking down the lyophobic groups by their finest structural details such as branching and unsaturation in the alkyl chain. Such extremes, however, can introduce unnecessary complications in any discussion of structure–performance relationships, especially since surfactant systems consisting of several isomers or homologues are the rule rather than the exception. All subsequent discussion will adhere to what seems to be becoming the most widely accepted classification system based upon the general chemical type of the lyophobic and solubilizing groups.

When discussing the commercial aspects of surfactant technology, especially with regard to the raw materials sources, it is common to refer to materials based on their original starting materials – petroleum-based “synthetics” or “natural” oleochemical-based materials. While such a classification may be useful from economic or sociopolitical points of view (natural being “better” than synthetic), the complex natures of such materials make it very difficult to illustrate the role of chemical structures in determining surfactant properties. While modern, extremely sensitive analytical procedures available today may be able to differentiate between nominally identical products derived from agricultural or petrochemical feedstocks, the functional impact of such differences is unlikely to be evident in the use phase of the surfactant life cycle. Later discussions, therefore, will be couched more in terms of chemical structure than of source. It should always be kept in mind, however, that nominally identical surfactants derived from different raw materials might exhibit differences in activity as a result of different isomer distributions.

In the following discussions, the previously introduced scheme of four primary surfactant classes has been employed, based on the nature of the principal solubilizing group. Subclassifications are developed for specific hydrophobic or hydrophilic groups. Among the various books and reviews on surface activity and surfactants, there is often some disagreement as to the proper classification of amphoteric or zwitterionic materials. Some authors prefer to class such materials as nonionic because of their net electrical neutrality; however, the presence of discrete charges on the molecules, their potential sensitivity to environment (pH, temperature, etc.) in some cases, and personal preference cause me to favor the use of a separate classification. In the final analysis, the materials themselves could care less what we may call them; it is the manifestation of their chemical nature in solution and at interfaces that concerns us. As long as we have a firm concept of the chemical structures involved and their effects on the activity of a surfactant, nomenclature can be safely relegated to a position of secondary importance.

2.5 Anionic Surfactants

The largest class of surface-active materials in general use today fall in the anionic classification, constituting 70–75% of total worldwide surfactant consumption. The major subgroups of this class are the alkali carboxylates or soaps, sulfates, sulfonates, and, to a lesser degree, phosphates. The variety of anionic materials available arises primarily from the many types of hydrophobic groups that can be modified by the addition of the proper anionic species. The overwhelming predominance of the anionic class of surfactants in economic importance is illustrated in Table 2.2. In 2015, approximately 65% of the total weight of surfactants consumed in the more industrialized countries was of the anionic variety.

Soaps derived from animal and vegetable fats and oils were the only surfactants available to mankind for thousands of years. The historical and economic advantage of the fatty acid soaps has always been their ready availability from natural, renewable sources. The exact properties of a given carboxylate soap will depend on the source of the raw material. The tallow acids (derived from animal fats), for example, are generally composed of oleic acid (40–45%), palmitic acid (25–30%), and stearic acid (15–20%). The materials derived from coconut fatty acids are usually composed of 45–50% C₁₂ acids, 16–20% C₁₄, 8–10% C₁₆, 5–6% oleic acid, and 10–15% of materials of less than 12 carbons. Additional materials are derived from the tall oils (50–70% fatty acids and 30–50% rosin acids). In almost all the carboxylic acid materials, the acid is neutralized to the sodium or potassium salt, although amine salts are popular for some specific applications. As already mentioned, the major disadvantages of the carboxylic acid soaps are that they are very sensitive to the presence of di- and trivalent cations; high salt concentrations of any type; low pH, which produces

Table 2.2 Approximate consumption of various surfactant types in the major industrialized areas in 2000 ($\times 10^5$ metric tons).

Surfactant type	Amount	% of total
Anionic (total)	4284	65
Nonionic (total)	1845	28
Other (amphoteric, cationic, etc.)	461	7
Total, all surfactants	6590	100

water-insoluble free fatty acids; and low temperatures. They also have surface adsorption characteristics that make them hard to rinse off, leaving a generally undesirable “soapy” feel on the skin or cloths that may produce itching when dry.

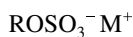
The development of synthetic surfactants began when the functional or perceived shortcomings of the classical soaps in many modern industrial processes requiring surfactant action became apparent. Those same modern processes, especially in the field of organic synthesis, made it possible and practical to produce better alternatives on an industrial scale. It was found, for example, that the sensitivity of soaps to changes in pH and the presence of polyvalent ions could be overcome by the addition of another solubilizing group to the molecule. From an early synthetic point of view, the most readily accessible functionalities were the sulfonic acids and sulfuric acid esters of long-chain alkyl groups. Beginning with the development of the so-called turkey red oil used in the dyeing industry in the latter part of the nineteenth century, surfactants based on either sulfate esters or sulfonic acid salts have dominated the field.

The rapid growth in the availability of alternate raw materials after World War II led to the development of well-characterized synthetic surface-active materials to meet the needs of the new technological world. Because of their utility and relative ease of manufacture, the sulfate and sulfonate surfactants continue to lead the way, although many classes of ionic and nonionic compounds have been investigated and developed in the hope of finding a “super surfactant” with the surface activity and economic attractiveness to dominate a large portion of the market for such materials. The literature on the development of new surfactants, both academic and industrial, represents a wealth of useful knowledge for the surfactant chemist or the user in need of a solution.

2.5.1 Sulfate Esters

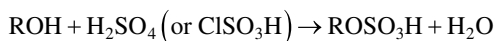
The neutralized organic esters of sulfuric acid, closely related chemically to the sulfonic acid salts to be discussed later, exhibit a number of significant differences in the chemistry of their preparation, in their hydrolytic stability after preparation, and in their ultimate activity as surfactants. Some of those differences are related to the different natures of the chemical linkages between the hydrophobic tail of the sulfates (carbon–oxygen–sulfur) and that of the sulfonates (carbon–sulfur). Such seemingly minor differences in chemical structure lead to differences in the polarizability of the head group, different degrees of ion binding in solution, and different degrees of hydration, all of which may alter the surfactant characteristics of the materials. Since the most widely studied surfactant, sodium dodecyl sulfate or SDS, is a member of the sulfate ester family, we will, out of deference to the “king,” discuss that family first.

As the name implies, the sulfate ester surfactants contain a sulfuric acid ester group, which acts as the solubilizing group. Usually encountered as the alkali or ammonium salts, this class of materials has the generic formula

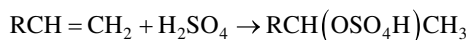


where R is one of the hydrophobic groups described earlier. While the best known members of this class are the simple straight-chain aliphatic materials such as SDS, many more complex structures are known and have found wide application.

The synthesis of the sulfate esters usually involves either the esterification of an alcohol with sulfuric acid, sulfur trioxide, or chlorosulfonic acid or the addition of sulfuric acid across a double bond:



or



While the reactions as written appear quite simple, it must be remembered that the substrates for such processes are often mixtures of isomers or even functionalities, so that the resultant product may be much more complex than indicated. When agriculturally derived feedstocks are employed, the material being sulfated may contain both saturated and unsaturated alcohol functionalities. In such cases, any double bonds present normally will not be attacked until all the alcohol has reacted. As the substrates become more complex, as in the case of hydroxy fatty acids and esters, the rather harsh conditions of the reaction process can lead to other side reactions.

The surfactant properties of sulfated materials are sensitive to the starting material composition and conditions of reaction. While it is possible to characterize the general physical properties of such materials, a precise interpretation of experimental measurements of surface activity may be difficult. In the following chapters that are concerned with such measurements and interpretations, the properties of complex mixtures generally will be inferred from those of “pure” analogous materials. It must always be kept in mind, however, that an industrial-grade product may exhibit some characteristics significantly different from a laboratory purified analog.

The sulfate ester surfactants have attained their great technical importance based on several factors including (i) good water solubility and surface activity, as well as reasonable chemical stability, (ii) a relatively simple synthetic pathways amenable to low-cost commercial production, and (iii) readily available starting materials from a number of agricultural and petroleum sources.

2.5.1.1 Fatty Alcohol Sulfates

Prior to World War II, fatty alcohols became available from the catalytic hydrogenation of natural fatty acids derived from vegetable and animal by-products. The alcohol was then sulfated by reaction with chlorosulfonic acid and neutralized with alkali. The first of the commercial alcohol sulfate surfactants came onto the market in Germany and slowly gained popularity in the first half of the twentieth century. More recently, alcohols have been produced by various catalytic processes using ethylene as the starting material. The Ziegler process, for example, yields even-numbered alcohols, essentially equivalent to those found in the natural fatty acids. Any desired chain length can be produced, and the alcohols can be blended in almost any proportion. Myristic acid ($n\text{-C}_{13}\text{COOH}$), a starting material for the preparation of myristyl alcohol, for example, is not found in great quantities in natural sources but can be prepared in unlimited amounts by this process.

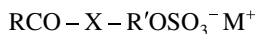
Alcohols prepared by the “oxo” process are slightly branched and always contain a portion of secondary alcohols. Being secondary alcohols, they are not as easily sulfated as the primary isomers, and since they contain both even and odd chain lengths, the physical properties of the resulting surfactants may differ somewhat from those of the natural and Ziegler process alcohols.

In addition to more varied alcohol sources, product quality is improved by the use of gas phase SO_3 as the sulfating agent instead of the harsher chlorosulfonic and sulfuric acids. As a result, the surfactants generally have a lighter color and less sodium sulfate as a contaminant.

2.5.1.2 Sulfated Fatty Acid Condensation Products

In addition to the simple alkyl sulfate esters discussed above, there exists substantial patent literature related to more complex sulfate esters of condensation products. Such materials would include linking groups such as amides, ethers (and polyethers), esters, and amines.

Condensation products containing sulfate groups and condensation linkages have the general structure



where X can be oxygen (ester), NH or alkyl-substituted N (amide), and R' is alkyl, alkylene, hydroxy-alkyl, or alkoxyalkyl. Such compounds have been found to exhibit good wetting and emulsifying characteristics and are often used in cosmetics and personal care products because of their low skin irritation properties relative to the simple alcohol sulfate esters. A number of such structures have been described in the patent literature and have gained significant commercial attention.

The major members of this class of sulfated surfactants are the sulfated monoglycerides and other polyols and sulfated alkanolamides. The sulfated monoglycerides are generally prepared by the controlled hydrolysis and esterification of triglycerides in the presence of sulfuric acid or oleum. The process and the properties of the final products are, as might be expected, sensitive to conditions of temperature, reaction time, and reactant concentrations. Because of the natural availability of the starting materials for such processes, the sulfated monoglycerides have a great deal of commercial potential in the so-called developing countries of Latin America, Asia, and Africa, where triglycerides from plant and animal sources may be more readily available than the more expensive petroleum-based raw materials. Surfactants based on coconut oil have historically been popular and can be found in a number of commercial products.

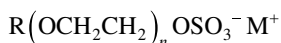
Other sulfated esters of polyols have been suggested as surfactants and have, in fact, been extensively patented. Sulfated monoesters of ethylene glycol and pentaerythritol have received some attention in that regard. They have not, in general, found much commercial acceptance, probably because of the hydrolytic instability of the ester linkage.

The drawbacks of the alkanol esters can be overcome by the use of the alkanolamide linkage. Hydroxyalkylamides can be conveniently prepared by the reaction of hydroxyalkylamines with fatty acids or esters and by the reaction of epoxides with fatty amides. Since the latter process can result in the formation of a number of products, it is not generally employed for the preparation of materials where a single derivative is desired. The resulting materials are generally more hydrolytically stable than the corresponding ester, with increased stability being obtained if the amide linkage is separated from the sulfate group by more than two carbons. Such materials have been found to have good detergent properties when combined with soaps and are sometimes used in toilet bars and shampoos because of their low irritation.

2.5.1.3 Sulfated Ethers

Nonionic surfactants of the POE type, which will be discussed in a following section, generally exhibit excellent surfactant properties. The materials have been found to have two primary disadvantages, however, in that they are usually not good foam producers (an advantage in some applications such as automatic washing machines) and under some conditions give cloudy solutions, which may lead to phase separation. Fatty alcohol sulfates, on the other hand, generally have good foaming properties, but their more common sodium salts often do not produce clear solutions except at low concentrations. To achieve clarity, it is often necessary to use some cation other than sodium, which may increase costs or introduce other difficulties.

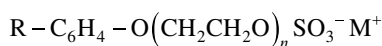
When a fatty alcohol is ethoxylated, the resulting ether still has a terminal —OH, which can subsequently be sulfated to give the alcohol ether sulfate (AES):



This class of surfactant has been extensively investigated because it has the potential to combine the advantages of both the anionic and nonionic surfactant types. In general, the ethoxylation of the fatty alcohol is not carried sufficiently far to produce a truly water-soluble nonionic surfactant; usually five or fewer molecules of ethylene oxide are added, and the non-sulfated material is still of limited solubility in water. The water insoluble nonionic material, however, can then be sulfated with chlorosulfonic acid or SO_3 and neutralized, usually with sodium hydroxide, to yield the desired product. Other counterions may be employed by slight modifications of the reaction or by the use of alternative reaction schemes.

The sodium salts of the ether sulfates have relatively limited water solubility. They do not usually perform as well as many other anionic surfactants as wetting agents, but their foaming properties are considerably better. They have found extensive use in shampoo formulations, and, in combination with other anionic and nonionic surfactants, they are being used more for household dish-washing detergents.

Lightly ethoxylated alkylphenols can also be sulfated to produce surfactants with the general formula



The sulfated alkylphenol ethoxylates have found use in toilet soap preparations, but their main success has been in the area of light-duty household detergent liquids. In the preparation of such materials, however, the basic alkyl polyether phenol starting material has two possible reaction pathways: attack at the terminal $-\text{OH}$ (to produce the desired sulfated polyether) and sulfonation of the benzene ring. Since the product intended in this case is the sulfated ether, it is desirable that no ring sulfation occur. A complete exclusion of ring attack can be achieved by several techniques, including the use of sulfamic acid as the sulfating agent. Such a procedure produces the ammonium salt, which may in some instances be more useful than the sodium analogue.

The figure given for the degree of ethoxylation of an alcohol, the “ n ” in the chemical formula, is only an average. The low values of generally used in the sulfated products mean that there may be significant quantities of non-ethoxylated alcohol or phenol in the mixture as well as some molecules with significantly more OE units, which will be sulfated in subsequent steps and which can have a significant impact on the characteristics of the final product.

2.5.1.4 Sulfated Fats and Oils

A final class of sulfated alkyl surfactants is that of the sulfated fats and oils in which the sulfate esters are obtained by the treatment of a variety of hydroxylated or unsaturated natural fats and oils with sulfuric or chlorosulfonic acids. These materials represent the oldest types of commercial synthetic surfactants, dating back to the original turkey red oils. Because of the nature of the starting materials and processes of preparation, the sulfated fats and oils are chemically heterogeneous materials whose properties are very sensitive to their history. In fact, the preparation of such materials may rightly be considered to be more art than science. They will contain not only sulfated glycerides similar to those discussed above but also sulfated carboxylic acids and hydroxycarboxylic acids produced by hydrolysis of the starting materials. With the increased availability of more chemically pure surfactant materials, the use of the sulfated fatty oils has decreased considerably. They do still have their uses, however, especially where purity is not a major concern and cost is important.

From a technological point of view, the aliphatic sulfate ester surfactants have not attained a wide range of applicability, even though they are heavily used in areas where their properties fit

the need. With few exceptions they are used as detergents or wetting agents, or both, with good detergency being favored by the longer hydrocarbon chains and good wetting by the shorter homologues. The more chemically pure materials, especially the *n*-alkyl sulfates such as SDS, have found application in a number of areas related to emulsion polymerization and, of course, represent probably the most intensively characterized family of surfactants known.

2.5.2 Sulfonic Acid Salts

Although chemically similar to the sulfate esters, the sulfonic acid salt surfactants can differ considerably in properties and chemical stability. As with the sulfates, there exists a wide variety of hydrophobic groups that control the properties and applications of these materials. Some of the major groups or sources are discussed briefly below.

Some sulfonic acids were no doubt produced in the early sulfuric acid processing of the “sulfated oils” in the late nineteenth century. The first commercially available sulfonate surfactants, however, were produced as a result of raw materials shortages in Germany during World War I. Some short-chain sodium alkyl naphthalene sulfonates were developed and despite relatively poor detergent properties were found to be good wetting agents and are still used as such today. The sulfonates in this series have also found use as emulsifying agents and dispersants in several agricultural and photographic applications. The postwar expansion of the chemical industries of Great Britain, Germany, and the United States led to the development of a number of new synthetic sulfonate surfactants, which have since gained a significant share of the commercial market.

Materials that are related through the sulfonate group include the aliphatic paraffin sulfonates produced by the photochemical sulfonation of refinery hydrocarbons, petroleum sulfonates derived from selected petroleum distillate fractions, olefin sulfonates, *N*-acyl-*N*-alkyl taurines, sulfosuccinate esters and related compounds, alkyl aryl sulfonates, and lignin sulfonates, which are a by-product of the paper manufacturing process. While complete coverage of the class would be prohibitive, some of the most important types are described below.

2.5.2.1 Aliphatic Sulfonates

The simple aliphatic sulfonic acids and their salts are represented by the general formula $R-SO_3^- M^+$, where *R* is a straight- or branched-chain, saturated or unsaturated alkyl or cycloalkyl group of a sufficient size to impart surface activity and M^+ is hydrogen, an alkali metal ion, an organic cationic species, or, in rare cases, a polyvalent metal ion. The classic example of these materials would be sodium dodecyl sulfonate, not to be confused with its sulfate ester cousin SDS. As with the sulfates, appreciable surface activity is not attained until the length of the alkyl chain reaches eight carbons, and water solubility becomes a problem around C_{18} . Since they are salts of strong acids, the members of this class of surfactants do not generally show a sensitivity to low pH conditions and are considerably more stable to hydrolysis than the analogous alkyl sulfates. While the monovalent salts of the sulfonic acids are quite water soluble and exhibit good wetting and detergency properties, their calcium and magnesium salts are of limited solubility; as a result, such materials are not generally favored as detergents, especially for use in “hard water” situations.

Paraffin sulfonates, or secondary *n*-alkyl sulfonates, are mostly a European product prepared by the sulfoxidation of paraffin hydrocarbons with sulfur dioxide and oxygen under ultraviolet irradiation. They are used in applications similar to those of the linear alkylbenzene sulfonates (LABS) discussed below. It has been suggested that the paraffin sulfonates have higher water solubility, lower viscosity, and better skin compatibility than the LABS of comparable chain length, although

any such direct comparison must be qualified because of the distinctly different chemical and isomeric contents of the two classes of materials.

Petroleum sulfonates are prepared by the reaction of selected petroleum refining fractions with sulfuric acid or oleum. The raw materials are a complex mixture of aliphatic and cycloaliphatic isomers, and the resulting surfactants are equally complex. As a result, the exact properties of the products may not always be sufficiently consistent to allow their use in critical applications. They are, however, relatively inexpensive and have found significant use in tertiary oil recovery, as frothing agents in ore flotation, as oil-soluble corrosion inhibitors, as components in dry-cleaning formulations, and as oil/water emulsifying agents in metal cutting oils. Although they are inexpensive, they usually have a dark color and may often contain a significant amount of non-sulfonated hydrocarbon as a contaminant.

α -Olefin sulfonates are prepared by the reaction of sulfur trioxide with linear α -olefins. The resulting products are a mixture of alkene sulfonates and primarily 3- and 4-hydroxyalkane sulfonates. The α -olefin sulfonates are gaining acceptance for use in detergents and other consumer products because of their tendency to be less irritating to the skin and their greater biodegradability.

The alkyl sulfonate salts can be prepared in a number of ways and have been the subject of considerable patent activity. They have not, however, achieved the widespread utility of the corresponding sulfates, primarily because of the easier and more economical methods for the synthesis of the esters and their better detergent activity. Special members of this class, the perfluoroalkyl sulfonates, have gained a great deal of attention because of their enhanced and sometimes unique surfactant properties. Although such materials are expensive relative to the analogous hydrocarbons, their great stability in harsh conditions and their enhanced surface activity at very low concentrations make the extra cost palatable in specialized applications. These materials will be discussed more fully in the subsequent discussions of fluorinated surfactants in general.

2.5.2.2 Alkyl Aryl Sulfonates

The sulfonation of aromatic nuclei such as benzene and naphthalene is a time-honored and reasonably well understood organic chemical process. Simple sulfonated aromatic groups alone are not able to impart sufficient surface activity to make them useful in surfactant applications, however. When the aromatic ring is substituted with one or more alkyl groups, which in some cases can be rather small, the surface-active character of the molecule is greatly enhanced. This class of materials has become exceedingly important as a major fraction of the commercially important anionic surfactants.

Particularly important members of this family are the alkylbenzene sulfonates (ABS) and the LABS. The ABS family, as mentioned earlier, is based on highly branched tetrapropylene alkyl groups that resist biodegradation processes, something that is less of a problem with the linear alkyl analogues.

Although usually sold as the sodium salt, LABS materials can be very useful in nonaqueous systems if the nature of the cation is changed. The calcium salt, for example, can have significant solubility in some organic solvents, as do many of the amine salts, especially that of isopropylamine. Since the materials are the salts of strong sulfonic acids, they are essentially completely ionized in water, as are the free sulfonic acids. They are not seriously affected by the presence of calcium or magnesium salts or high concentrations of other electrolytes, and they are also fairly resistant to hydrolysis in the presence of strong mineral acids or alkali. While the sodium salts are not soluble in organic solvents, the free acid may be neutralized with amine bases to produce materials with high organic solubility.

Most of the commercially available alkylbenzene materials contain a C_{12} alkyl chain with the points of attachment to the benzene ring being a random distribution along the chain. Materials with longer alkyl chain lengths (C_{13} – C_{15}) are also available and have the potential advantage of being somewhat more soluble in organic solvents. A disadvantage of the LABS is that they are somewhat resistant to biodegradation under anaerobic conditions, although they pose no problem under aerobic conditions.

Members of the LABS family of surfactants exhibit several characteristics that explain their predominance in many surfactant applications. Not only do they show outstanding surfactant properties in general, but they are also derived from raw materials that are relatively easy to obtain and less expensive than those from which the other main types of surfactant are prepared. The main source of the LABS is the petroleum industry, and it will probably remain the most economical raw material for these materials for some time to come.

As mentioned earlier, this class of materials is the product of the Friedel–Crafts alkylation of benzene with a long-chain alkyl group, the prime example being dodecylbenzene. This compound may be derived from an alkyl chloride containing an average of 12 carbon atoms. The source of the alkyl chain may be a particular cut of petroleum distillate or a synthetic hydrocarbon chain obtained by the controlled oligomerization of a low molecular weight alkene – generally ethylene or propylene.

Because of the comparatively high cost of chlorine and the co-production of hydrogen chloride, the use of olefin feed stocks has become the preferred route to these materials. For that reason, the propylene tetramer was for many years the primary source of the alkyl group. When the change to linear alkylbenzenes occurred for reasons of improved biodegradability, straight-chain olefins were frequently used.

Although the aromatic nucleus in surfactants is usually benzene, it is also possible to use toluene, xylene, phenol, and naphthalene. The oldest of the sulfonate-based, synthetic surfactants, in fact, are the alkyl naphthalene sulfonates developed in Germany during World War I. Although comprising a relatively small part of the total surfactant market, they have shown considerable staying power for use as wetting agents for agricultural applications and paint formulations and have long been used for the preparation of emulsions of dye precursors in color photographic products. When the nucleus employed is naphthalene, the alkyl side chain may be as small as propyl; however, in that case, single substitution does not produce a material with useful surfactant properties, although some surface activity does result. To obtain significant wetting and detergency effects, the naphthalene nucleus must contain two or more propyl groups. If the chain length of the alkyl group is increased, the surfactant properties improve correspondingly until, above C_{10} , solubility problems begin to arise.

As the molecular weight of the alkyl chain attached to the aromatic nucleus increases, it becomes important to limit the final product to a single-chain substitution. In general, as the alkyl chain increases in length, water solubility decreases, and surfactant activity reaches a maximum and then begins to decrease. In practice, for benzene derivatives, dodecylbenzene sulfonate has generally been found to exhibit the best overall balance of desirable surfactant characteristics.

In the science and technology of surfactants, the requirements placed upon a given material or process can vary greatly in different parts of the world. Except in the case of specially prepared and purified materials for basic scientific investigations, reference to a material such as sodium dodecylbenzene sulfonate implies a material whose average molecular weight and structure is that of the $C_{12}H_{25}C_6H_4SO_3^-Na^+$. The industrial product, in fact, will never be a single homogeneous material. If the feedstock is the propylene tetramer, it is possible that the material will be contaminated with small amounts of ethylene and butylene, which, during polymerization, will produce

various amounts of the trimer and pentamer of each, along with the trimer and pentamer contaminants from the propylene itself.

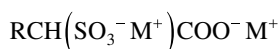
Mixed oligomers of all the ingredients are also possible, so the final product will contain a distribution of molecular weights and isomers. When the isomers are coupled to the benzene nucleus, more isomeric possibilities arise, leading to a product containing an enormous variety of structures. With such a wide variety of molecular species present in the basic feedstock for sulfonation, it becomes difficult to reproducibly manufacture materials with the identical component distribution and surfactant characteristics. It has become common, therefore, to distill the alkylbenzene prior to sulfonation and employ the cuts with molecular weights in the ranges of 233–245 and 257–265, depending upon the manufacturer and the intended use for the final material.

The compound prepared from the lower molecular weight fraction is commercially referred to as dodecylbenzene and the higher as tridecyl benzene. The so-called tridecyl material is actually a mixture of mostly C_{12} and C_{14} isomers, the exact mixture depending upon the manufacturer. The tridecyl benzene sulfonate, in general, shows better detergent properties and better foaming in soft water, whereas dodecylbenzene sulfonate has a lower cloud point and better viscosity behavior in liquid detergent formulations.

The change to linear alkylbenzene brought certain changes in surfactant properties. Since the alkyl portion is linear in the primary feedstock, there are no significant problems with different branched isomers at that stage, although some homologues will undoubtedly be present. When reacted with benzene, the coupling between olefin or alkyl chloride can occur at any of the positions along the alkyl chain except at the termini so that a number of isomeric alkyl substitutions will result. Branching of the alkyl groups, however, will not occur. It has been shown that the surfactant properties of the product depend very strongly on the final position of the phenyl group along the alkyl chain. It is to be expected, then, that nominally equivalent ABS and LABS surfactants will exhibit different properties. The effects of substitution patterns will be covered in later chapters concerned more directly with the surface-active properties of surfactants from a structural and physicochemical standpoint.

2.5.2.3 α -Sulfocarboxylic Acids and Their Derivatives

The α -sulfocarboxylic acids are represented by the general formula



in which R is CH_3 or a longer alkyl chain and M is hydrogen or a normal surfactant cation. The lower molecular weight analogues such as those derived from propionic, butyric, and possibly slightly longer acids are not sufficiently hydrophobic to be surface active. However, if the free carboxylic acid is esterified with a fatty alcohol of proper length, usually C_8 – C_{18} , the resultant materials will generally perform well as surfactants. A typical example of such a material is sodium dodecylsulfoacetate:



The esters of sulfoacetic, α -sulfopropionic, and α -sulfobutyric acids with long-chain alcohols are highly surface active but have found little general application because of their relatively high cost. They have several specialty applications, especially in personal care products such as toothpastes, shampoos, and cosmetics. Some have also been approved for use in conjunction with mono- and diglycerides in food applications.

The α -sulfocarboxylic acids of higher molecular weight, especially lauric, palmitic, and stearic acids, are highly surface active. It is generally found that the water solubility of the unesterified α -sulfo acids decreases as the length of the carbon chain increases, as might be expected. Less obvious are the observed effects of the state of neutralization of the carboxylic acid and the nature of the counterion on solubility. In the case of the free acid sulfonate, solubility is found to increase in the order $\text{Li} < \text{Na} < \text{K}$, while the solubility of the neutralized di-alkali salt increases in the opposite order. The use of alkylammonium counterions is also found to increase the solubility of a given chain length material.

The presence of the free acid or carboxylate salt combined with the sulfonate group has suggested the use of such materials as corrosion inhibitors when applied to metal surfaces, which can form strong salts or complexes with carboxylic acid groups. Related applications would be in ore flotation. The materials have also found some utility as viscosity reducers in liquid detergent formulations. The free carboxyl group offers the possibility of additional derivatization, such as esterification or amidation. Esterification of the carboxyl group has usually been found to increase the water solubility of a given acid, as long as short-chain alcohols are employed. Unlike many esters, those of the α -sulfocarboxylic acids are generally resistant to hydrolysis, although they are readily biodegradable under both aerobic and anaerobic conditions:



The surface properties of a series of α -sulfocarboxylic acid esters, in which the chain length of the acid (R_1) was varied from C_2 to C_{18} and that of the alcohol (R_2) from C_1 to C_{16} , were found to vary considerably with the location of the sulfonate group along the chain. Esters of short-chain alcohols and long-chain acids exhibit critical micelle concentrations roughly equivalent to those of the analogous alkyl sulfate surfactant of the same hydrocarbon chain length. Such materials show good detergent properties, while materials with equal carbon numbers, but with longer alcohol and shorter acid groups, were superior wetting agents with larger **cmc**'s (see Chapter 4). The α -sulfocarboxylic acid esters have found application as lime-soap dispersants, components in dry-cleaning formulations, detergent powders, mineral flotation, and soap bars.

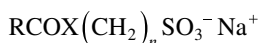
Esterification is not the only method of derivatizing the carboxyl functionality, and it is not surprising that amides and *N*-alkyl amides of the α -sulfo acids have also received extensive attention in the surfactant patent literature. The α -sulfoalkanolamides have the general structure



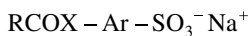
where R_1 can be H or an alkyl group. The simple amide materials generally have similar surface properties to the analogous sulfo acid, while the *N*-alkyl-substituted materials closely correspond to the sulfo-esters in their solubility. While they are not widely used as industrial surfactants, they are receiving some attention for use in personal care formulations.

2.5.2.4 Miscellaneous Sulfo-Ester and Amide Surfactants

The sulfo-esters and amides discussed in the preceding section are those in which the two functionalities were located on adjacent carbon atoms, a situation that imparts some special properties to the resultant surfactant molecules. A second class of related materials is that in which the two groups are more widely separated. General examples of such compounds would be



and



in which R is the usual alkyl chain of 8–18 carbon atoms, $n = 2-4$, X is O, NH, or *N*-alkyl, and Ar is an aromatic nucleus such as benzene or naphthalene.

The fatty acid esters and amides having the general structures above were some of the earliest and most commercially successful materials that adequately overcame the problems of hard water and acid sensitivity that plagued many surfactant applications. The sulfoethyl ester of oleic acid was the first of a line of such materials. As with many esters, however, those materials showed some tendency to hydrolyze in solution and have been pretty much replaced by the more stable amide derivatives. The presence of the amide nitrogen not only enhanced the hydrolytic stability of the sulfo-acid materials, but it also provided a locus for the further customization of the surfactant molecule and, therefore, modification of its surface properties. By the judicious choice of the variables R, X, n , etc., a wide range of wetting, foaming, detergency, and related properties could be designed into the surfactant. As many as 15 different sulfo-esters and amides of this family are currently in wide commercial use.

The *N*-acyl-*n*-alkyl taurines are prepared by the condensation of taurine or *N*-alkyl taurine (usually methyl or ethyl) with a fatty acid:



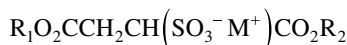
The resulting material will usually exhibit solubility, detergency, foaming, and other properties very similar to those of the corresponding fatty acid soap. They have the distinct advantage, however, of being much less sensitive to low pH, high electrolyte concentrations, and the presence of di- and trivalent ions. They are also stable to hydrolysis and show good skin compatibility. As a result they are very popular for use in toilet soaps, bubble baths, and shampoos. They are also excellent as wetting agents.

Related to the sulfo-acid esters and amides are materials derived from sulfonated polycarboxylic acids. Such polyacids include succinic, itaconic, phthalic, and isophthalic acids and the tricarbalylates. The presence of several carboxylic acid groups in these materials opens the way for the preparation of a variety of multifunctional surfactant molecules.

The most commonly encountered members of this class of materials are the sulfosuccinate and sulfosuccinate esters and diesters. Those materials, which have excellent wetting, emulsifying, dispersing, and foaming properties, are relatively cheap and easy to prepare. As a result, they have gained wide acceptance for many applications.

The mono- and diesters of sulfosuccinic acid, especially the sodium di-2-ethylhexyl ester, have found wide application as wetting agents and emulsifiers in paints, printing inks, textiles, agricultural emulsions, and photographic materials. They can be prepared to have good solubility in either water or organics, so many desirable properties can be designed into the molecule. The synthesis is straightforward and will produce materials essentially free of inorganic salt contaminants, unlike many other members of the sulfonate class of surfactants. Their major disadvantage is that the ester group is susceptible to hydrolysis in either alkaline or acidic solutions.

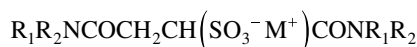
The sulfosuccinate esters have the general structure



where $R_1 = R_2$ for most diesters and $R_2 = H$ for the monoester. They were first commercialized under the trade name “Aerosols.” The diesters with R_1 being C_9 or less generally have good water solubility, although the di-*n*-octyl diester does have some solubility problems in water at room temperature. The branched-chain esters usually have higher water solubility than the straight-chain analogues.

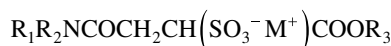
The higher alkyl analogues of these materials are somewhat unique in that they have good solubility in a wide variety of organic solvents and undergo apparent micelle formation in many non-aqueous systems. A possible disadvantage of the sulfosuccinate esters is that they do undergo significant hydrolysis under both acidic and basic conditions. The secondary alcohol esters are more stable in this regard than the primary analogues, especially under basic conditions.

Related to the sulfosuccinic diesters are the sulfosuccinamides, succinimides, and succinamates, which may show some advantage in stability but usually require more harsh conditions for formation. The sulfosuccinic diamide materials are prepared in a manner similar to that of the diesters from maleic anhydride or the free acid and a primary or secondary amine, followed by the addition of sodium bisulfite across the double bond to give materials of the general structure



where R_1 is an alkyl group of suitable size to impart the desired surface activity and R_2 may be H or a second alkyl group.

The sulfosuccinamates can be obtained by the reaction of maleic anhydride with a primary or secondary amine to form the monoamide, followed by esterification and sulfonation to the desired product



in which the R's have their usual meaning.

The sulfosuccinimides may be of two varieties, one analogous to the previously mentioned succinic acid derivatives, where the sulfonate group is added across the double bond of maleic acid and subsequently reacted to produce the cyclic imide. The second variety requires a different synthetic approach, since the locations of their hydrophilic and hydrophobic groups are reversed from those of the succinic acid derivatives. In this case, the starting material is a 2-alkyl, alkenyl, etc., succinic anhydride, which is reacted with the appropriate sulfoalkylamine to produce the amide acid, followed by dehydration to the imide. Similar reaction schemes can be used to prepare di- and higher polyesters and amides of malonic acid, itaconic acid, and other polycarboxylic acids.

Unlike the sulfosuccinic acid derivatives, sulfopolyesters and amides and imides of the phthalic acids and other sulfonated aromatic carboxylic acids can be prepared by the direct esterification, amidation, etc. of the corresponding acid.

There are a variety of potential surfactant structures that can be prepared from the other polycarboxylic acids available to the synthetic chemist. Their properties as surfactants have received a great deal of attention because surface activity and solubility in water and organic liquids can be varied almost continuously by the proper choice of the esterifying alcohol. As mentioned earlier, the use of shorter chain alcohols ($<C_9$) results in materials with substantial water solubility, with branching favoring higher solubility. As the alcohol chain passes through C_8 , significant oil solubility can be achieved so that those compounds become useful as non-aqueous surfactant systems. Surfactant characteristics such as wetting power also vary with chain length, with longer chains usually resulting in a greater effectiveness as a wetting agent. Other surfactant properties of these materials will be discussed in later chapters.

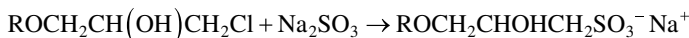
Because the sulfosuccinates and sulfosuccinamates have shown excellent wetting, dispersing, emulsifying, and foaming properties, they have found a wide variety of applications in industry. Their applications range from use in lubricating oils, ink dispersions, mineral ore flotation, and oil emulsion breakers to stabilizers for emulsion polymerizations and emulsifiers and coating aids in photographic products. Some members of this family have also found extensive use in shampoos, toilet bars, and other cosmetics because of their low skin irritation and for ingestion as stool softeners.

2.5.2.5 Alkyl Glyceryl Ether Sulfonates

The alkyl glyceryl ether sulfonate class of surfactants represented by the general formula



were first synthesized in Germany relatively early in the twentieth century. However, there are very few data published about their specific properties, other than the information available in the patent and trade literature. An early patent described the reaction of epichlorohydrin with a fatty alcohol to produce the chloroether, which was subsequently treated with sodium sulfite to yield the desired sulfonate salt:



The specific details of the reaction pathways to these materials can be quite complex, not in the chemistry involved, but in the conditions necessary to obtain a commercially useful product and process. The major problems are control of the formation of diether and higher ether from the epichlorohydrin and the removal of unreacted starting materials and by-products from the final material.

Patent references to the alkyl glyceryl ether sulfonates describe them as efficient wetting, foaming, and dispersing agents, with improved water solubility and stability to acids and bases. The materials are, however, inherently more expensive than most other sulfonates and therefore have not received a great deal of interest in most high volume, low-cost applications. They have found extensive use only in specialty areas where the added cost for the specific advantages of such materials can be tolerated.

2.5.2.6 Lignin Sulfonates

Lignin sulfonates are, technically, low molecular weight polymers containing a witch's brew of primary and secondary alcohols, phenols, and carboxylic acid functionalities. They are prepared by the sulfonation of lignin by-products of pulp and paper manufacture, followed by neutralization to the sodium, calcium, or ammonium salt. The resulting materials are useful as dispersing agents for solids and oil-water emulsions and as stabilizers for aqueous dispersions of dyes, pesticides, and cement. They are very inexpensive relative to other materials and are very low foaming. They have the disadvantages of being highly colored, insoluble in organic solvents, and relatively ineffective at lowering surface tensions.

2.5.3 Carboxylate Soaps and Detergents

Their long and well-documented history notwithstanding, it is important to include some mention of the classical carboxylate soaps and related materials in this review of anionic surfactant classes. While a complete history of soap technology will not be presented, a few special carboxylic acid

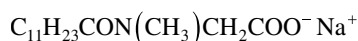
salts have been prepared that are claimed to be superior to the classical soaps in both surface activity and stability to hard water and pH variations, as well as providing a number of functional advantages in product formulations. Such materials often contain additional polar groups such as esters and amides, different fatty acids compositions, or non-fatty acid components that impart greater solubility and stability to the neutralized soap product. This class of materials includes not only normal esters and amides of fatty acids but also those of the amino acids. Because the starting materials for such materials are often mixtures, the final products are usually complex and may often be poorly characterized.

The natural fatty acid soaps derived from tallow (animal fat) continue to form an important group of surfactants even though their portion of the market has tended to decline relative to the synthetics. The salts of the coconut oil acids and some acids derived from oil seed sources, on the other hand, have found increased use in hard water applications and liquid hand soaps, where high soap concentrations are desired. The improved performance of coconut oil soaps probably results from their higher content of the lower molecular weight C_{12} and C_{14} acids (60–70%) versus the tallow soaps (80–95% C_{14} or greater).

Other sources of carboxylate salt surfactants include those derived from (i) tall oil by-products of wood and paper manufacture, (ii) condensation products of fatty acids with sarcosine (2-(*N*-methylamino)-ethanoic acid, $(CH_3)HNCH_2COOH$) and other amino acids and proteins, and (iii) fatty acid esters of common hydroxy acids such as lactic, tartaric, citric, and succinic acids.

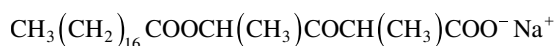
The tall oil soaps are particularly attractive because they are very inexpensive. They are actually complex mixtures of fatty acids and rosin acids, which are difficult to characterize and control. The presence of the rosin acids in these materials generally imparts better water solubility as well as enhanced surfactant properties. Because of their complex nature and difficulties in obtaining sufficiently “clean” materials, the tall oil soaps have generally found use only in the most tolerant areas of heavy-duty industrial cleaning and within the processes from which they are derived.

Condensation products of fatty acids with amino acids to produce materials such as *N*-lauryl sarcoside



have been shown to possess several properties that make them useful in personal care products. They are often less sensitive to hard water and low pH than the tallow soaps and, because of their structures, are nonirritating to skin and eyes. Many of the amino acid derivatives are nontoxic and have found uses in oral applications such as toothpastes and mouthwashes. Additional uses can be found in such diverse areas as antistatic agents and lubricants for food packaging polymers, textiles, petroleum recovery, metal processing fluids, carpet cleaners, and photographic emulsions. Acylated proteins derived from leather and bone also show good detergent properties and perform well as fabric softeners and “control” agents in shampoos.

Esters of fatty acids, primarily stearic and palmitic, and distilled monoglycerides with lactic, tartaric, citric, succinic, and related hydroxy acids have found wide application as emulsifiers and improvers in the food industry. Sodium or calcium salts of esters of stearic acid with lactic acid (sodium stearyl-2-lactylate or SSL)



and diacetyltartaric acid esters of monoglycerides (DATEM)



are widely used throughout the world in the production of bread and other bakery products. The “natural” character of such products derived from lactic acid (an α -hydroxy acid) has led to their occasional use in skin and hair care products. Because of the nature of the starting materials for such products, they are rather complex mixtures of compounds ranging from free fatty acid salts to low molecular weight polymers and cyclic isomers of the corresponding hydroxyl acids. Those types of surfactants will be revisited in more detail in Chapter 13.

2.5.4 Phosphoric Acid Esters and Related Surfactants

The esters of phosphorus-based acids constitute a relatively uniform group of anionic surfactants that can fill a special role in the overall scheme of surfactant applications. The esters and diesters of phosphoric acid have the general formula



where the R group is a usually a long-chain alcohol or phenol. The materials may be obtained as the free acid ($\text{M} = \text{H}$) or sodium or amine salts. In fact, they are generally found as a mixture of mono- and dibasic phosphates. The surfactant properties of the alkyl phosphates vary. They have been reported to be somewhat superior to related sulfates and sulfonates in some applications because of their low foaming characteristics, good solubility in water and many organic solvents, and resistance to alkaline hydrolysis. However, their performance as detergents seems to be inferior in most cases. The phosphate esters have the general disadvantage of being more expensive than sulfonates and sulfates; but wider solubility and good activity in harsh environments have made them useful in dry-cleaning formulations, highly alkaline cleaners, and various emulsion formulations.

Useful variations of the alkyl phosphate surfactants are those in which a POE chain is inserted between the alkyl and phosphate ester groups. Such materials are usually found to exhibit only slight anionic character, having properties more in common with the nonionic analogues. An advantage of the addition of the phosphate group to the nonionic is that the resultant material will quite often have better solubility in aqueous electrolyte solutions. Additional advantage can be gained from the fact that the pour point, the temperature at which the nonionic surfactant solidifies, can be significantly decreased by phosphorylation. These materials are somewhat limited by the fact that they hydrolyze in the presence of strong acids, although their stability to strong alkali, like that of the simple phosphates, is quite good. The wetting, emulsifying, and detergent properties of these surfactants are generally better than similar phosphate surfactants not containing the added solubilizing groups.

Lecithins, glyceryl esters containing two fatty acid residues and one phosphate ester (usually as phosphatidylcholine), constitute one of the oldest of the commercially important phosphoric acid derivative surfactants. However, since they contain nitrogen and are normally either nonionic or amphoteric, they are not discussed further in this section. Additional phosphorus-containing surfactants include derivatives of phosphonic and phosphinic acids.

Although not comprising a particularly large portion of the total surfactant market, on either a weight or a dollar basis, the phosphorus-containing surfactants have carved themselves a substantial niche in many industrially important applications. That importance is emphasized by the large

number of commercially available materials. The organophosphorus surfactants exhibit a number of useful surface properties related to emulsification, wetting, detergency, solubilization, etc. They have also found a number of significant uses as a result of non-surfactant-related characteristics such as antistatic and lubrication properties, corrosion inhibition, and fuel additives. Recent ecological problems have led to a reduction in the use of phosphate-containing formulations for many applications, especially laundry detergents; however, their unique properties and general safety make them a useful tool in the overall repertoire of surfactant types available today.

The foregoing discussion of anionic surfactants only touches the tip of the iceberg in relation to the exceedingly wide variety of materials available. More comprehensive coverage of the topic is available in several volumes cited in Bibliography for this chapter. Leaving the pursuit of more detail to the interested reader, we now turn our attention to the positively charged cationic family of surfactants.

2.6 Cationic Surfactants

Cationic surfactants first became important when the commercial potential of their bacteriostatic properties was recognized in 1938. Since then, the materials have been introduced into hundreds of commercial products, although they do not approach the importance of the anionic materials in sheer quantity or dollar value. Currently, cationic surfactants play an important role as antiseptic agents in cosmetics, as general fungicides and germicides, as fabric softeners and hair conditioners, and in a number of bulk chemical applications. Many new applications for cationic surfactants have been developed since World War II, so these compounds can no longer be considered to be specialty chemicals; rather, they truly fall into the category of bulk industrial surfactant products.

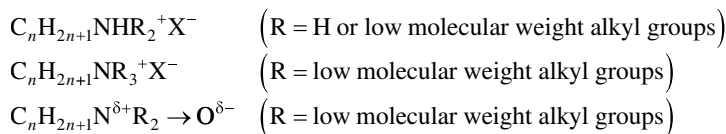
Relative to the other major classes of surfactants, namely, anionics and nonionics, the cationics represent a relatively minor part of worldwide surfactant production, probably less than 10% of total production. However, as new uses and special requirements for surfactants evolve, their economic importance can be expected to continue to increase.

Commercial cationic surfactants, like their anionic and nonionic counterparts, are usually produced as a mixture of homologues, a point that must always be kept in mind when discussing physical properties and applications of such materials. As previously noted, slight variations in the chemical structure or composition of the hydrophobic group of surfactants may alter their surface active properties, leading to the possibility of important errors in the interpretation of results and in performance expectations. That possibility holds true for all surfactant classes and will be emphasized repeatedly throughout this work. When the sources of hydrophobic groups for cationic surfactants are natural fatty acids such as coconut oil or tallow, there may be significant variations in both chain length and the degree of unsaturation in the alkyl chain. When the alkyl group is derived from a petrochemical source, the components may be found to vary in molecular weight, branching, the presence of cyclic isomers, and the location of ring substitution in aromatic derivatives.

Pure cationic surfactants such as cetyltrimethylammonium bromide (CTAB) have been used extensively for research into the fundamental physical chemistry of their surface activity. Such investigations have led to a vast improvement in our basic understanding of the principles of surfactant action. Because of the significant differences in purity and composition between commercial and research-grade materials, however, care must be taken not to overlook the effects of such differences on the action of a given surfactant in a specific application.

Prior to the availability of straight-chain, petroleum-based surfactants, the sole sources of raw materials for cationic surfactants were vegetable oils and animal fats. All those materials could be

considered to be derivatives of fatty amines of one, two, or three alkyl chains bonded directly or indirectly to a cationic nitrogen group. The most important classes of these cationics are the simple amine salts, quaternary ammonium compounds, and amine oxides:



There are two important categories of cationic surfactants that differ mainly in the nature of the nitrogen-containing group. The first consists of the alkyl nitrogen compounds such as simple ammonium salts containing at least one long-chain alkyl group and one or more amine hydrogen atoms and quaternary ammonium compounds in which all amine hydrogen have been replaced by organic substituents. The amine substituents may be either long-chain or short-chain alkyl, alkylaryl, or aryl groups. The counterion may be a halide, sulfate, acetate, etc. The second category contains heterocyclic materials typified by the pyridinium, morpholinium, and imidazolinium derivatives as shown in Figure 2.3. Other cationic functionalities are, of course, possible, but are much less common than these two major groups.

In the pyridinium and other heterocyclic amine surfactants, the surfactant properties are primarily derived from the alkyl group used to quaternize the amine. As a variation to that approach, however, it is possible to attach a surfactant-length alkyl (or fluoroalkyl) group directly to the heterocyclic ring and quaternize the nitrogen with a short-chain alkyl halide. Many commercial cationic surfactants with the general structures $\text{R}-(\text{CH}_2)_5\text{NH}^+\text{R}'\text{X}^-$ and $\text{R}-(\text{CH}_2)_5\text{N}^+\text{R}'\text{X}^-$, where R is the surfactant-length hydrophobic group and R' is a short-chain alkyl or hydroxyalkyl chain, are available. As is the case with the anionic materials, the structures of such materials are limited mainly by the skill and imagination of the preparative organic chemist.

Some types of amphoteric surfactants (to be discussed below) in which the nitrogen is covalently bound to a group containing an anionic (e.g. $-\text{CH}_2\text{CH}_2\text{SO}_3^-$) or potentially anionic (e.g. $-\text{COOH}$) functionality are also classed as cationic in some publications; however, under the classification

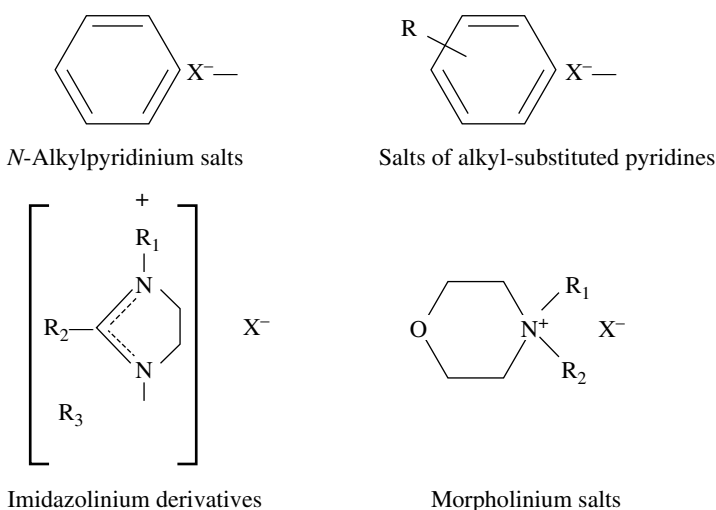


Figure 2.3 Typical structures of heterocyclic cationic surfactants ($\text{X}=\text{Cl}^-$, Br^- , CH_3COO^- , SO_4^{2-} , etc.).

scheme employed in this work, such materials are covered in a separate category. The examples above represent the simplest types of cationic surfactants. Many modern examples contain much more complex linkages; however, the basic principles remain unchanged.

The economic importance of the cationic surfactants has increased significantly in recent years because of some of their unique properties. Most cationics are biologically active in that they kill or inhibit the growth of many microorganisms. They have also become extremely important to the textile industry as fabric softeners, waterproofing agents, and dye-fixing agents. Because many important mineral ores and metals carry a net negative charge, the cationic surfactants are also useful in flotation processing, lubrication, and corrosion inhibition, and they are gaining importance as surface modifiers for the control of surface tribological properties, especially electrostatic charge control. Since the hydrophobic portions of the cationic surfactants are essentially the same as those found in the anionics, individual discussion of those groups is not repeated here.

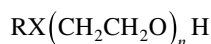
2.7 Nonionic Surfactants

Although the two surfactant types discussed so far can be characterized by the existence of a net electrical charge on the molecule that imparts a required degree of solubility, such a situation is not a fundamental requirement for the existence of surface activity in water. In fact, there may be several very good reasons for having surfactant materials that are electrically neutral. Some of the most important advantages can include a significantly lower sensitivity to the presence of electrolytes in the system, a reduced effect of solution pH, and the synthetic flexibility of being able to design the required degree of solubility into the molecule by the careful control of the size of the hydrophilic group.

An interesting characteristic of many nonionic surfactants, especially the POE family, is that they exhibit an inverse temperature–solubility relationship. That is, as the solution temperature is increased, their solubility in water decreases. The phenomenon is attributed to a disruption of specific interactions, in this case, hydrogen bonding, between the water and the POE units in the molecule. The temperature at which components of the POE surfactant begin to precipitate from solution is defined as the “cloud point.” In general, the cloud point of a given family of surfactants (with the same hydrophobic group) will increase with the average number of OE groups.

2.7.1 Polyoxyethylene-Based Surfactants

Of all the nonionic surfactant classes available, which are few, but increasing in number, the POE are easily the most numerous and the most important technically. These materials have the general formula

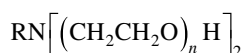


where R is normally a typical surfactant hydrophobic group, but may also be a hydrophobic polyether such as polyoxypropylene, and X is O, N, or another functionality capable of linking the POE chain to the hydrophobe. In most cases, n , the average number of OE units in the hydrophilic group, must be greater than 5 or 6 to impart sufficient water solubility to make the materials useful. The “average” nature of n should be emphasized, since the reaction pathways leading to the product will always result in a distribution of molecular weights. Pure, homogeneous samples of materials with low n , usually less than about 10, can be prepared, but at great expense. Such materials

have little technical significance beyond the information gained by studying the effects of stepwise addition OE groups.

The most common reaction pathway to the POE surfactants is the reaction of ethylene oxide with a hydrophobic material containing at least one reactive hydrogen. Alternative routes include the reaction of the hydrophobe with a preformed POE chain or the use of ethylene chlorohydrin instead of ethylene oxide. Neither of the latter reactions has achieved industrial importance for mass surfactant production, although the use of preformed glycols can be a useful route to homogeneous surfactant samples.

As mentioned above, the reacting hydrophobe must contain at least one active hydrogen, as in the case of alcohols, acids, amides, mercaptans, etc. If primary amines are used, there exists the possibility of forming double-chain surfactants of the form



In such materials, the values of n for each POE chain will be averages and may be quite different, so the complexity of the resulting product will likely be greater than that of the single-chain analogue.

Some of the specific effects of the variables (R, X, N, etc.) on the surfactant properties of the POE surfactants will be seen in more detail in the following chapters. In general, however, it is usually found that a number of the properties of materials with the same hydrophobic group and varying POE chain lengths will change in a regular, predictable manner. By way of illustration, the following patterns have been determined for n -dodecyl-POE surfactants:

- 1) Water solubility increases regularly as the number of OE groups is increased from 3 to 16.
- 2) The surface tension of aqueous solutions of the materials decreases regularly over the same composition range.
- 3) The interfacial tension between aqueous solutions and hydrocarbons reaches a maximum at around $n = 5$ and decreases from there.
- 4) Foaming power reaches a maximum at about $n = 5$ or 6 and remains relatively constant from that point.
- 5) Other technologically important characteristics of these materials such as detergency, wetting power, dispersing ability, etc. are also found to vary regularly with OE content.

2.7.2 Derivatives of Polyglycerols and Other Polyols

Polyol surfactants, because of their general biocompatibility and their relatively low cost, in most cases, have found a number of important uses, including many that require strenuous testing and clearance by the US Food and Drug Administration and other governmental agencies throughout the world. Their principal areas of impact include foods and food emulsions, pharmaceuticals, cosmetics, and agricultural applications of pesticides and herbicides. Additional uses include lubrication, cutting oils, detergents, dry-cleaning fluids, and miscellaneous specialized applications.

Like the POE-based surfactants, compounds derived from the condensation products of hydrophobic groups containing an active hydrogen and glycerol or other polyols constitute an important family of nonionic surfactants. Represented by the general structure



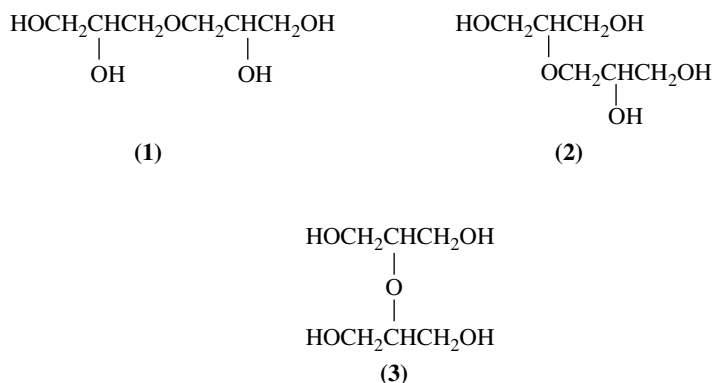


Figure 2.4 Potential isomers of polyglycidyl addition products.

where R and n have the usual significance, R' may be H or OH , and X may be CH_2 (an ether), CO_2 (an ester), or other linkages. Some such materials, especially the polyglycerols, are more complex mixtures than those previously discussed because of the potential for branching in the oligomerization reaction. There are three possible isomers of diglycerol (Figure 2.4), and each subsequent addition of a glycerol unit increases the isomeric possibilities in the final product. A completely random distribution of isomers will not be obtained because of differences in the reactivity of the various hydroxyl groups. The mixture will, however, be so complex that accurate analysis is difficult.

There are two generally encountered routes to the synthesis of surfactant-grade polyglycerols. One involves the polymerization of glycidol to form the polyglycerol followed by esterification with a surfactant-class fatty acid. The alternative method is the reaction of glycerol with a hydrophobic group containing a reactive hydrogen in a way similar to the preparation of the POE surfactants. Sufficiently reactive materials include alcohols, amines, acids, phenols, mercaptans, and amides.

The products of the reactions above have been shown to have good wetting and dispersing properties, and they are good emulsifiers in many cases. They have the advantage that they are generally nontoxic and are employed in a number of useful food-related applications. These would include food emulsions, such as margarine, and moisturizing additives for breads and other baked goods. A disadvantage of such materials is that the reaction process can result in the formation of a significant amount of non-surfactant polyglycerol, which is difficult to remove from the mixture. In addition, there seems to be a practical limit of about 10 glycerol units, above which the polyglycerol becomes intractable and reaction with the hydrophobic group becomes difficult.

An interesting member of the polyol surfactants that is even more complex is the family of polyglycerol polyricinoleates that are prepared by the high temperature, low-pressure oligomerization of castor oil or ricinoleic acid with glycerol. Ricinoleic acid is a hydroxy acid that on reaction produces an ester unit containing three to five ricinolate units esterified to a polyglycerol of up to 10 glycerol units. Such compounds have been found to have very useful effects in chocolate manufacture and in whipped dessert products.

Other classes of polyol surfactants have as their starting materials polyhydroxy compounds with two to six hydroxyl units per chain. Those hydrophilic groups include sugars, ethylene and propylene glycol, and other related materials. The surfactants are usually prepared by the esterification of fatty acids with the desired polyol, normally resulting in the formation of mixtures of mono-, di-, and often polyalkyl esters. The commercial products, therefore, may be complex mixtures of

compounds whose final properties must be determined by the careful control of feedstock composition and reaction conditions. Relatively pure monoglyceride esters (>90% α -mono) may be obtained by molecular distillation. Distilled monoesters of propylene glycol are also important in the food industry.

Esters of fatty acids with sorbitan are frequently ethoxylated to various degrees. The esters and ethoxylated esters (the well-known Spans, Tweens, Polysorbates, etc.) form a very important family of nonionic materials for use in many applications such as foods, cosmetics, and pharmaceuticals.

A number of surfactants based on the fatty acid esters of sucrose and other sugars are now becoming important because of the more “natural” character of the polyol versus POE and related materials. These “sugar detergents” are reported to have good detergent properties and to be non-toxic. In contrast to the POE family of surfactants, the sugar-based materials exhibit few solubility problems below 100 °C and appear to be very effective in mixed micelle formation in combination with anionic surfactants such as sodium dodecyl sulfate. As the ester, the sugar surfactants have some problems with regard to hydrolytic stability in acid media. Alternative linkages that have been suggested to overcome such problems include amides and urethanes.

A major drawback of the sucrose ester surfactants is the difficulty of synthesis due to the lack of mutual solubility between the sugar and the hydrophobic components, usually fatty acids. To obtain a commercially viable process, a good solvent for all components such as dimethylsulfoxide (DMSO) must be used. To make the final product meet FDA standards, the level of residual DMSO must be extremely low requiring rigorous purification, implying high production costs. Nevertheless, the advantages of the family of products have led to their commercial productions in limited quantities.

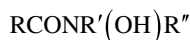
2.7.3 Block Copolymer Nonionic Surfactants

An interesting class of nonionic surfactants that has developed as a result of advances in block polymerization techniques is that of the polyalkylene oxide copolymers. Such materials exhibit many interesting and useful properties that have allowed them to carve out a special niche in the surfactant formulation world. Although they are relatively low molecular weight materials as polymers go, they are much larger than normal surfactant molecules and for that reason will be discussed in more detail in Chapter 9.

2.7.4 Miscellaneous Nonionic Surfactants

A number of technologically important nonionic surfactants do not fall into any of the main categories discussed so far. These include the alkanolamides derived from fatty acids, amine oxides, sulfoxides, and phosphine oxides, and others too numerous to cover adequately in a brief overview of surfactant technology. Such materials are reported frequently in the patent literature and are cited in several works cited in the Bibliography.

Perhaps the most commercially important family of surfactants falling in this category consists of the fatty alkanolamides given by the general formula



where the R group is a fatty acid or mixture of acids, while R' can be a simple short-chain hydroxyalkyl (e.g., $-\text{CH}_2\text{CH}_2\text{OH}$) or a more complex ether, amine, or other such structure

containing hydroxyl group. The R'' can be H, alkyl, or the same as R' to yield a diol surfactant. The fatty alkanol amides are found in a wide variety of products, especially where high foaming and foam stability are perceived to be advantageous, either in the action of the formulation or for esthetic reasons. Prime examples of such applications would be shampoos and dishwashing liquids. Such materials have also been found to be generally hypoallergenic and readily biodegradable, resulting in their increased use in cosmetic and other formulations.

Amine oxides are prepared by the oxidation of tertiary amines with peroxides or peracids to yield materials that, while possessing a formal charge separation on the nitrogen and oxygen atoms, behave as non-electrolytes:



The R , R' , and R'' groups may be alkyl, aryl, or any of several other structures, with at least one being a fatty acid residue. Most commonly, the R' and R'' will be CH_3 .

Additional classes of nonionic surfactants can be found in the patent and other specialized literature. In many cases the materials described are of little practical significance, but they should not be totally ignored, especially when very special or unique applications and properties are being considered.

2.8 Amphoteric Surfactants

The family of surfactants commonly referred to as “amphoterics” are surface-active materials that contain, or have the potential to form, both positive and negative functional groups under specified conditions. Their definition as a separate class of surfactants has historically been somewhat controversial, since they may be electrically neutral and their general properties under many conditions make them functionally similar to some nonionic surfactants. For purposes of discussions related to chemical structures, however, they have been separated into a distinct family. In the final analysis, a surfactant by any other name is still a surfactant, so too much importance should not be placed on nomenclature.

Although amphoteric materials represent only a small portion of total worldwide surfactant production, their market position is increasing significantly because of the unique properties such materials can impart to a formulation. It is particularly important that they often show considerable synergism when employed with other classes of surfactants. Their nature can make them especially useful in applications requiring biological contact, for example, in “no tears” baby shampoos. In addition, for uses that might involve the presence of charged polymeric species, the “dual” nature of the materials reduces or eliminates the possibility of undesirable polymer-surfactant interactions (see Chapter 9).

There exists a rather large group of organic functionalities that hold the potential for producing amphoteric surfactants, but there are four classes of materials most often encountered, namely, imidazoline derivatives, betaines and sulfobetaines, amino acid derivatives, and lecithin and related phosphatides. Charge-separated compounds such as amine oxides and sulfoxides, mentioned in the nonionic section, could easily be included in the amphoteric classification; however, the more intimate nature of their charge separation, as compared to the internal salts to be discussed here, seems to justify their inclusion in the nonionic category.

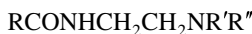
It may be noticed that the discussion of amphoteric surfactants of the first three classes allows for considerable overlap as far as chemical structures are concerned. Surfactants that can be

considered to be amino acid derivatives may be prepared via the imidazoline intermediate or by some more direct route as described below. The betaines, on the other hand, are nothing more than a special subclass of amino acid derivatives in which the amino group has been quaternized, again resembling a subclass of the imidazoline-derived materials. Clearly, an unequivocal distinction between the general types of amphoteric surfactants is impossible. A detailed description of the wide range of possibilities that exist in this class of materials is given in the works cited in the Bibliography. A brief description of some of the main groups of amphoteric surfactants will illustrate the general chemical nature of this family of materials.

2.8.1 Imidazoline Derivatives

Imidazoline-derived surfactants represent one of the most commercially important classes of amphoteric surfactants. Although mentioned in the patent and surfactant literature as early as 1940, they received little commercial attention until the early 1950s, when it became evident that they possessed a number of potentially useful properties, including a significantly greater mildness to skin and eyes than other surfactants. As a result, the imidazolines have developed a significant place in the cosmetics and personal care products market. The growing availability of these materials as a result of their importance in the cosmetics industry has led to their application in a number of other unrelated fields.

Most commercially important imidazoline-derived amphoteric surfactants can be described as fatty acid/aminoethyl ethanolamine condensates of the general structure



where R is the fatty acid residue and R' and R'' can be any of several functionalities to be described below. The free tertiary amine can be further alkylated to produce a quaternary ammonium compound possessing a permanent positive charge. Most commercial imidazoline surfactants are prepared in a two-step process. First a fatty acid is condensed with a polyamine such as ethylenediamine or aminoethyl ethanolamine, with the loss of approximately 2 mol of water to yield a cyclic imidazoline. The second step is the alkylation of the imidazoline with an alkylating agent containing the anionic portion of the final molecule and ring opening to give the final product.

Although there are a wide variety of chemical structures possible, four main classes can be found in most commercially available materials. Those classes, as well as their predominant ionic forms and ionization characteristics, can be summarized as follows:

Class 1: Amine/carboxylic acids (not to be confused with the amino acid derivatives to be discussed in following sections) containing both free amine ($-\text{NR}_2$) and free acid ($-\text{COOH}$) functionalities. These materials will be cationic at low pH ($-\text{N}^+\text{R}_2\text{H} + -\text{COOH}$), isoelectric near neutral pH ($-\text{N}^+\text{R}_2\text{H} + -\text{COO}^-$), and anionic at high pH ($-\text{NR}_2 + -\text{COO}^-$).

Class 2: Quaternary ammonium/carboxylic acids. These materials contain a permanent cationic site ($-\text{N}^+\text{R}_3$) as well as the carboxyl group. At low pH they will, of course, be cationic. At slightly alkaline pH they will become isoelectric and remain so. They can never become anionic in the way the class 1 materials can.

Class 3: Amine/sulfonic acids (or sulfate ester). Having the strong acid sulfonic acid group, which is highly ionized even at low pH, these materials will form internal salts and will be essentially isoelectric in very acidic media. As the pH is raised to the alkaline side, the protonated amine is neutralized to yield a net anionic species. These materials are essentially the opposite of the class 2 surfactants.

Class 4: Quaternary ammonium/sulfonic acids (or sulfate esters). Possessing both the permanent cationic charge of the quaternary ammonium group and the highly ionizing strong acid, these materials will be isoelectronic over most of the pH range, except at very low pH under conditions where ionization of the acid may be suppressed.

These classifications represent the most fundamental members of this family of surfactants. It should be noted that the betaine and sulfobetaine surfactants discussed in the following section are in fact special members of classes 2 and 4. A number of additional structural modifications commonly encountered in commercial products add to the diversity of the materials and properties that can be obtained.

Most commercial carboxylated imidazoline surfactants are actually mixtures of classes 1 and 2 above, while the sulfated materials are combinations of classes 3 and 4. The carboxylated materials will usually have a buffering action in solution so that the native pH will be slightly alkaline. The class 3 and 4 materials possess slightly less buffering capacity but will lie just to the acidic side.

As mentioned above, the increased importance of the imidazoline-derived surfactants stems primarily from their mildness and low toxicity. The extent of their use in shampoos and body care products has followed closely the overall increase in the use of such products worldwide. Their amphoteric nature also makes them useful in a wide range of water types, ranging from hard to soft water and high to low pH's. Such flexibility makes them useful in cleaning formulations that will see a variety of conditions.

The variable electronic characteristics of the amphoteric surfactants also make them useful in textile applications where antistatic and "softening" properties under various conditions and on different fabric types are advantageous. Treatment of various metal surfaces is also facilitated by the ambivalent nature of such materials, leading to their use in metal treating and finishing products.

2.8.2 Surface-Active Betaines and Sulfobetaines

Betaine is a naturally occurring material, first identified in the nineteenth century, having the chemical structure of trimethylaminoacetate:

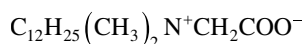


The compound is an internal salt that, in its natural form, has most of the characteristics of a totally unionized material. When one (or more) methyl group(s) is replaced by a long-chain alkyl such as a fatty acid residue, materials with significant surface activity can result. Such materials are now commonly referred to as betaine surfactants.

The betaine surfactants can be considered to be special members of the ring-opened imidazoline surfactants. However, they do not exhibit many of the characteristics of other amphoteric surfactants, especially with regard to their solubility and electrical nature in alkaline solution. Even at high pH, the betaines do not acquire any significant anionic character, and they appear to maintain their good water solubility, even at the isoelectric pH. They are compatible with anionic surfactants at all pH's and do not appear to have problems of complex formation. The carboxyl-containing betaines have been found to form external salts in very strong acids (e.g. hydrochlorides in HCl), while the sulfobetaines do not do so. Members of this class of surfactants are generally insensitive to the presence of electrolytes and usually perform well in hard water.

The carboxyl betaines have found a number of commercial applications including use in textile processing as leveling and wetting agents, detergents, scrubbing compounds, antistatic agents, and fabric softeners. They have also found use as lime-soap dispersants and in detergent formulations, dry-cleaning fluids, and personal care products. The sulfobetaines seem to have gained much less attention commercially, although they have been found to be useful in a number of special areas such as the control of static charge in photographic films.

The use of the term “betaines” is, of course, not technically correct from a chemical nomenclature standpoint, even though Chemical Abstracts does maintain such a listing in its Chemical Subjects Index. The betaine surfactants may be found named according to the parent amino acid, from which they can, in principle, be derived. For example, the compound



could be named *dodecylbetaine*, *N-dodecyl-N,N-dimethylglycine*, or *dimethyldodecylammonioacetate* or *ethanoate*.

Probably the oldest and still most common route to the carboxybetaines is through the quaternization of long-chain alkyldimethyl tertiary amines with chloroacetic acid. A similar route can be employed to prepare the analogous sulfobetaines from 2-chloroethane sulfonic acid. Other synthetic pathways can be found in the references cited in the Bibliography.

2.8.3 Phosphatides and Related Amphoteric Surfactants

Phosphatidyl surfactants, of which the commercially popular materials referred to as “lecithins” are members, are generally composed of di-fatty acid, monophosphoric acid esters of glycerol combined with an amine containing radical such as ethanolamine or choline. Typically, their structure can be written as shown below (IV), in which R and R' have their usual meanings. The location of the phosphate ester on the terminal carbon is designated an α -phosphatide, while location internally would be designated as β . Because of their natural sources, the phosphatidyl or lecithin surfactants are normally found as rather complex mixtures, especially with regard to the nature of R and R'. In general, the natural lecithin will have one saturated and one unsaturated R-group, with the saturated group usually found at the α -position.

Natural lecithin generally has limited solubility in water. Having good oil solubility, these materials have found extensive commercial application as nonaqueous emulsifiers, dispersants, and wetting agents in such diverse areas as marine paints, inks, foods, and cosmetics. More water-soluble materials can be prepared by the enzymatic removal of the β -fatty acid group. Such materials are commonly referred to as “lysolecithin.”

Sources of lecithin range from egg yolks to many seed oils such as cottonseed, sunflower, and soybean, with soybean being the most common because of its relatively lower cost and greater availability. It is, of course, possible to prepare synthetic phosphatidyl surfactants; however, a number of practical pitfalls make such approaches difficult at best. The preparation of an unsymmetrical diester of phosphoric acid presents inherent difficulties, as does the fact that the amine functionality can lead to the formation of salts of phosphatidic acid. The inherent reactivity of the ester functionalities also can lead to extensive ester interchange during preparation.

The phosphatide family concludes the general summary of the main classes of surfactants that are commonly encountered by the scientist or technician venturing into the field of surfactants and surface activity. In the discussions above, no attempt was made to provide a comprehensive review of all the surfactant classes and subclasses and the seemingly infinite structural variations

that can arise in the design and synthesis of surfactant molecules. Just a few of the general references cited in the Bibliography represent thousands of pages and several volumes of material on the subject. In addition, a scan of each volume of Chemical Abstracts reveals a number of new materials being disclosed in the patent and academic literature. Even the miracle of modern electronic communications and information transfer does not allow one to remain constantly abreast of the changing world of surfactant science and technology. The following chapters represent an attempt to summarize as clearly and succinctly as possible the physicochemical ramifications of chemical structure in surface activity and the application of such phenomena to modern technological needs.

The reader is again reminded that no attempt is made to provide an in-depth theoretical review of surfactant activity at interfaces or an encyclopedic listing of the various properties of every surfactant known to man. Suitable references are provided for the reader desiring more information on any given subject.

3

Surfactant Chemical Structures

Putting the Pieces Together

In order to better understand much of the information in following chapters related to surfactant chemical structures and their effects on surface activity, it is useful to understand how they are put together. The following material, therefore, will give a quick look at some of the steps involved in the synthesis of many of the big players in the surfactant game. Synthetic details are not given as a question of space-time concerns, but anyone familiar with first year organic chemistry should find the material easy to follow.

3.1 Surfactant Building Blocks

In aqueous systems, by far the most important medium of surfactant applications, the hydrophobic group is usually a long-chain hydrocarbon or hydrocarbon-aryl group, although there are examples using halogenated, especially fluorinated, or oxygenated hydrocarbon or siloxane chains. The hydrophobic group is usually denoted in shorthand as R—, although if an aromatic group such as benzene or toluene is involved, it may be written R—Ar—. The linkage between the hydrophile and hydrophobe is almost always made through the aryl group. The hydrophilic group will be an ionic or highly polar group that can impart some water solubility to the molecule. The most useful chemical classification of surface-active agents is based on the nature of the hydrophile, with subgroups being based on the nature of the hydrophobe. The four basic classes of surfactants are defined in Table 3.1.

The definitions given in Table 3.1 are obviously very general. However, relatively small variations on a given structure can produce unique and potentially useful changes in the activity and utility of a basic chemical structure. The nature of the hydrophobic groups may be significantly more varied than for the hydrophile. Quite often they are long-chain hydrocarbon groups; however, they may include, but are not limited to, such varied structures as those shown in Table 3.2. In the structures, —S indicates an unspecified hydrophilic group.

The structures given in Table 3.2 are very generalized, and later chapters will illustrate more of the many possible, useful variations. With such a wide variety of structures available, it is not surprising that the choice of a suitable surfactant for a given application can become a significant problem in terms of making the best choice of material for a given application.

Economic considerations, in addition to questions of chemical functionality, must usually be addressed when choosing a surfactant system, since cost considerations often play an important role in the selection process. If the cost of the surfactant is significant compared with that of other

Table 3.1 Some basic defining characteristics of surfactant classes.

Surfactant class	Principle characteristics
Anionic	The hydrophilic group carries a negative charge such as carboxyl ($\text{RCOO}^- \text{M}^+$), sulfonate ($\text{RSO}_3^- \text{M}^+$), sulfate ($\text{ROSO}_3^- \text{M}^+$), or phosphate ($\text{ROPO}_3^- \text{M}^+$)
Cationic	The hydrophilic group carries a positive charge, as for example, the quaternary ammonium salts ($\text{R}_4\text{N}^+ \text{X}^-$), where “X” represents a halide or other negatively charged atom or group
Nonionic	The hydrophilic group carries no charge but derives its water solubility from highly polar groups such as polyoxyethylene ($-\text{OCH}_2\text{CH}_2\text{O}-$) _n , a sugar molecule, polyglycerol, or other polyol groups
Amphoteric	The hydrophilic group carries, or can potentially can carry, both a negative and a positive charge, such as the sulfo-betaines ($\text{RN}^+(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{SO}_3^-$) and <i>N,N</i> -dimethyldodecane-1-amine oxide ($\text{C}_{12}\text{H}_{25}-\text{N}^+(\text{CH}_3)_2-\text{O}^-$)

Table 3.2 Some of the more common surfactant hydrophobic groups or tails.

Hydrophobic group	Basic structure
Long, straight-chain alkyl groups	$\text{CH}_3(\text{CH}_2)_n-\text{S}$, ($n = \text{C}_{11}-\text{C}_{20}$)
Branched-chain alkyl groups	$\text{CH}_3\text{CH}(\text{CH}_3)-[\text{CH}_2\text{CH}(\text{CH}_3)]_n-\text{S}$, ($n \geq 3$)
Alkylbenzenes	$\text{R}-(\text{C}_6\text{H}_4)-\text{S}$, ($\text{R} = \text{C}_8-\text{C}_{15}$)
Alkyl naphthalene sulfonates	$\text{R}_2\text{C}_{10}\text{H}_5-\text{SO}_3^- \text{Na}^+$ ($\text{R} \geq 3$)
Fluoroalkyl groups	$\text{XCF}_2(\text{CF}_2)_n-\text{S}$, ($n > 5$, $\text{X} = \text{H}$ or F)
Polydimethylsiloxanes	$\text{CH}_3-(\text{O}-\text{Si}[\text{CH}_3]_2\text{O})_n-\text{S}$
Polyoxypropylene glycol ethers	$\text{HO}-[\text{CH}-(\text{CH}_3)-\text{CH}_2-\text{O}]_n-\text{CH}_2-\text{CH}-(\text{CH}_3)-\text{S}$
Rosin and other natural product derivatives.	
Various polymeric structures.	
Other miscellaneous structures depending upon the creativity of the synthetic chemist.	

components of a system, the least expensive material producing the desired effect usually will be chosen. Economics, however, cannot be the only factor, since the final performance of the system will be of crucial importance. To make a rational selection of a surfactant, without resorting to an expensive and time-consuming trial-and-error approach, the formulator must have some knowledge of:

- 1) The surface and interfacial phenomena that must be controlled to achieve the desired results.
- 2) The characteristic chemical and physical properties of the available surfactant choices.
- 3) Any special chemical or biological compatibility requirements of the system.
- 4) And under ideal circumstances, the relationships among the structural properties of the available surfactants and their effects on the pertinent interfacial phenomena.

Some more detail about the chemical reactions leading to basic surfactant families will illustrate the “simplicity” of the chemistry involved in most surfactant syntheses. The following chapters will also attempt to provide a foundation for making logical surfactant choices – or at least provide a good starting point and grounds for a good “educated guess.”

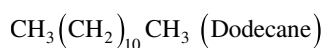
3.2 A Surfactant Family Tree

Assuming a “water-centric” point of view for the moment, surfactants, whether synthetic or of the “natural” fatty acid soaps family, are amphiphilic materials that tend to exhibit some solubility in water as well as some affinity for nonaqueous environments, as described. They are nature’s original bipolar chemical personalities, and we and the rest of our living world would not exist without them, because living cell capable of self-replication could not exist, at least as far as we know at the present time. As stated, such an ambivalent character as that required for surface activity occurs in materials that include two chemically distinct molecular groups or functionalities. For an aqueous system, the functionality that would be readily soluble in water is termed the *hydrophile*; the other functionality, the *hydrophobe*, would, under normal circumstances, be essentially insoluble in water. It is the “push me, pull you” conflict within the particular molecular structure that produces the unique and amazingly useful family of chemical beasts we know as surfactants.

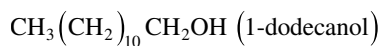
Chemically speaking, the hydrophilic group is usually, though not always, added synthetically to a hydrophobic material in order to produce a compound with some limited water solubility. The effectiveness of a given molecular structure as a surfactant will depend critically on the molecular balance between the hydrophile and the hydrophobe. Attaining the balance necessary to produce the desired result lies at the heart of surfactant science and technology, as does understanding the fundamental chemical principles leading to the observed phenomena. Several empirical schemes have been proposed for quantifying the critical balance between the two parts of surfactant molecules and relating that balance to the activity of the material in a given application. Some of those ideas will be covered in more detail in later chapters. For now, we will see what some relatively minor structural changes can do to the character of the simple hydrocarbon molecule *n*-dodecane.

3.2.1 The Many Faces of Dodecane

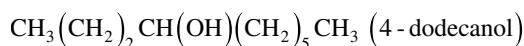
As the root of our surfactant family tree, we will consider the compound *n*-dodecane:



This material is a hydrocarbon with essentially no solubility in water and is just about as hydrophobic as one could want, in a practical sense. If one of the terminal hydrogen atoms is exchanged for an —OH group, the new material, 1-dodecanol, still has relatively low solubility in water, but it increases substantially relative to the parent hydrocarbon:



If the alcohol functionality is placed internally on the dodecane chain, as in 4-dodecanol, the resulting material will be similar to the primary alcohol but will have slightly different solubility characteristics:

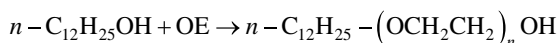


Solubility differences among chemical isomers will generally be evident in other functional modifications. The effects of the position of substitution on surfactant properties can be quite large and will be discussed in more detail in subsequent chapters.

Once formed, the alcohol can be sulfated to produce dodecane sulfuric acid ester, a compound with very high water solubility. When the sulfuric acid ester is neutralized with alkali, certain alkaline earth metals, or organic amines, the material becomes highly soluble in water and an excellent surfactant. It is, in fact, probably the most extensively studied and best understood surfactant known to science – sodium dodecyl sulfate or SDS:



If the 1-dodecanol is treated with ethylene oxide (OE) and base catalyst, the material obtained is a dodecyl polyoxyethylene (POE) polyether:



Such products can exhibit widely varying solubility characteristics, depending on the value of n , the number of OE groups added to the molecule. Because of the nature of the reaction, the value of n will be an average of a distribution of values. If $n = 10$, the material will be soluble in water and will show good surfactant properties. If n is as little as 5, its water solubility will decrease significantly, as will its usefulness as a surfactant. If n is taken to 20 or higher, high water solubility is attained, but most of the good surfactant qualities will be lost. For n less than 5, the material will have little significant water solubility.

If the original 1-dodecanol is oxidized to dodecanoic acid, also known as lauric acid, the resultant compound has very limited water solubility; however, when the acid is neutralized with alkali, it becomes water soluble, a classic soap:



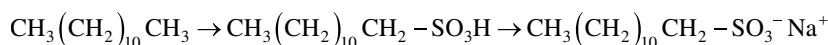
The alkali carboxylate will be a reasonably good surfactant for many applications, but if the hydrocarbon chain length were increased to 16 or 18 carbons, many of the surfactant properties would be even better, illustrating the importance of obtaining the proper balance between the hydrophilic and hydrophobic portions of the molecule. It should be pointed out that long-chain carboxylic acids such as dodecanoic acid used in surfactant manufacture are not synthesized, although they could be. They are more than sufficiently abundant and much more easily obtained from vegetable and animal fats and oils.

A major drawback to the use of the alkali soaps has always been their great sensitivity to their aqueous environment. The main components of so-called hard water are calcium, magnesium, and other divalent and trivalent cations. In the presence of such materials, the carboxylic acid soaps form salts of low water solubility, which precipitate to produce scummy deposits, commonly encountered as the “bathtub ring.” Their solubility in water is simply too low for the system to attain a high enough concentration to produce useful results. In nonaqueous solvents, on the other hand, the polyvalent salts of carboxylate soaps exhibit significantly enhanced solubility and perform admirably in many surfactant functions.

Carboxylate soaps are also strongly affected by changes in solution pH and temperature. Their solubility in water increases significantly with increases in temperature, as does their usefulness as cleaners, the reverse obviously being the case. The sensitivity of the carboxylate soaps to the presence of commonly encountered ions, their sensitivity to pH changes, and the decreased solubility in cold water were the driving forces for the development of synthetic surfactants that would not

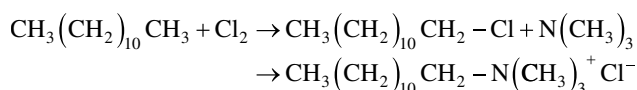
be so adversely affected by the common circumstances of hard water and cool washing temperatures, each highly detrimental to their effectiveness.

Continuing with the example of dodecane-based surfactant materials, the parent hydrocarbon can be sulfated to yield dodecane sulfonic acid, which closely resembles the sulfuric acid ester discussed previously and has similar miscibility with water:



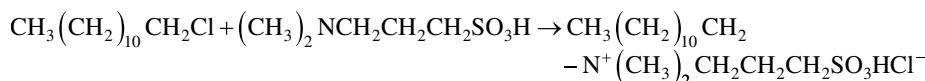
When neutralized with the proper base, the resulting material is an excellent surfactant. It should be noted that while the sulfonic acid is chemically related to the sulfonate ester, their solution and surfactant properties are not identical, so their potential applications may be different as well. The hydrocarbon sulfonates are generally more chemically stable than the sulfate esters, but the economics of their preparation is often an impediment to their widespread use.

If the original dodecane molecule was terminally chlorinated and reacted with trimethylamine:



the resulting compound would be dodecyl trimethylammonium chloride, a cationic water-soluble compound exhibiting some surfactant properties, but not generally as useful as the anionic analogues. The utility of such compounds is limited not so much by their surface activity as by their interaction with various oppositely charged components found in practical systems.

To this point we have covered three of the four general classes of surfactants mentioned in Chapter 1 – anionic, nonionic, and cationic. To produce an example of the fourth class, an amphoteric or zwitterionic surfactant, it is only necessary to react the dodecyl chloride prepared above with a difunctional material such as *N,N*-dimethyl-3-aminopropane-1-sulfonic acid:



The result is just one of several possible chemical types that possess the amphoteric or zwitterionic character of this class of materials. In strongly acidic media where the sulfonic acid is protonated, the molecule has a positive charge with a chloride counterion. If the pH is increased, the sulfonic acid becomes neutralized producing a sulfonate anion in the same molecule as the cationic nitrogen atom.

The number of chemical modifications of the dodecane or similar simple hydrocarbon molecules that can lead to materials with good surfactant characteristics is impressive. When molecules containing aromatic or other interesting functionalities are considered, the possibilities are limited primarily by the imagination and skill of the organic chemist – and by the time and money available for indulgence in creative molecular architecture.

In each example discussed above, an aqueous “solubilizing group” has been added to the basic hydrophobe to produce materials with varying amounts of useful surfactant characteristics. When one considers the wide variety of hydrophobic groups that can be coupled with the relatively simple hydrophiles so far discussed and add in more complex and novel structures, the number of combinations becomes impressive. When viewed in that light, the current existence of almost 2000 distinct surfactant structures does not seem quite so large.

3.3 Common Surfactant Hydrophobic Groups

Probably the most common hydrophobic groups used in surfactants are hydrocarbon chains having a total of 8–20 carbon atoms. Commercially there are two main sources for such materials that are both inexpensive (relatively speaking) and available in sufficient quantity to be economically feasible: biological sources such as agriculture and fishing and the petroleum industry (which is, of course, ultimately biological). Figure 3.1 indicates some evolutionary pathways from raw materials to final surfactant product. There are, of course, alternative routes to the same materials, as well as other surfactant types that require more elaborate synthetic schemes. Those shown, however, constitute the bulk of the synthetic materials used today.

Many, if not most, surfactant starting materials are, in fact, mixtures of isomers with their designation reflecting an average value of hydrocarbon chain length. In some cases, isomeric composition may be indicated in the surfactant name or description, while in others the user is left somewhat in the dark. The name “sodium dodecyl sulfate,” for example, implies a composition containing only C_{12} carbon chains. The material referred to as “sodium lauryl sulfate,” on the other hand, is nominally a C_{12} surfactant but will in fact contain some longer- and shorter-chain homologues. Each source of raw materials may have its own local geographic or economic advantage, so

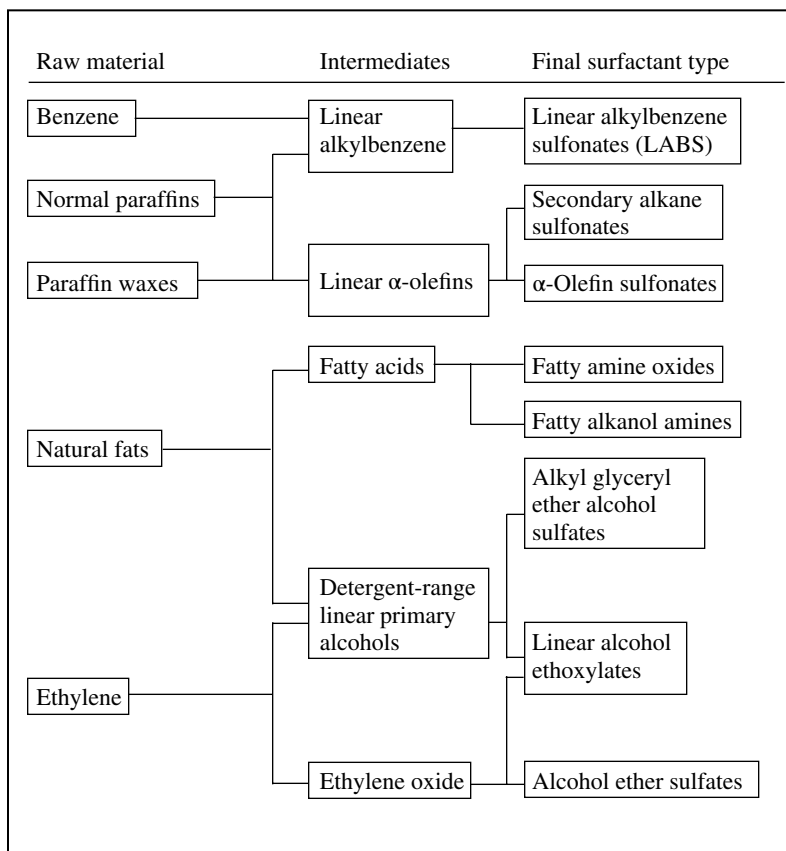


Figure 3.1 Evolutionary pathways for some of the more important types of hydrophobic groups of commercial surfactants.

nominally identical surfactants may exhibit slight differences in surfactant activity due to the subtle influences of raw material variations. Such considerations may not be important for most applications but should be kept in mind in critical situations.

3.3.1 The Natural Fatty Acids

One of the major sources of raw materials for the commercial production of surfactants is the oldest source, agriculture. Fats and oils (oleochemicals), products of nature's ingenuity and man's labor, are triglyceride esters of fatty acids, which can be readily hydrolyzed to the fatty acids themselves. A naturally occurring plant or animal fatty acid usually contains an even number of carbon atoms, so groups symbolized by an R in abbreviated nomenclature will contain an odd number that is one less than the corresponding acid. The carbons are linked together in a straight chain with a wide range of chain lengths, those with 16 and 18 carbons being the most common. The chains may be saturated, in which case the R group has the formula C_nH_{2n+1} , or they may have one or more double bonds along the chain. Hydroxyl groups along the chain are rather uncommon, but not unknown, especially in soaps made using castor oil (ricinoleic acid); other substituents are rather rare.

Commercially, the largest surfactant outlet for fatty acids is conversion to soap by neutralization with alkali. In a strict sense this may be considered to be a synthetic process, and soap therefore is a synthetic surfactant. However, common usage reserves the term "synthetic" for the more modern products of chemical technology that have been developed in the twentieth century and generally show improvements over the older soap technology. The chemical processes required for the modern surfactants and detergents are also usually much more complicated.

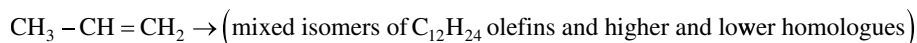
3.3.2 Paraffins or Saturated Hydrocarbons

The hydrophobic groups derived from the petroleum industry are principally hydrocarbons, coming originally from the paraffins of crude oil. The chain lengths most suitable for detergent hydrophobes, C_{10} – C_{20} , occur in the crude oil cuts boiling somewhat higher than gasoline, namely, kerosene, and above. The main components of kerosene are saturated hydrocarbons ranging from $C_{10}H_{22}$ to $C_{15}H_{32}$, ordinarily containing 10–25% of straight-chain homologues. There are larger amounts of branched-chain isomers present, in addition to quantities of saturated cyclic derivatives, alkylated benzene, naphthalene, and minor amounts of other polycyclic aromatics.

The paraffins have the disadvantage of being chemically unreactive, so direct conversion to surfactants is somewhat difficult. As discussed above, substitution of one or more hydrogen atoms with halogen offers a pathway to some surfactant systems, but manufacturing complications can be an impediment. It is usually necessary to synthesize the surfactant by way of some more reactive intermediate structures, commonly olefins, alkylbenzenes, or alcohols. These compounds contain reactive sites that are more easily linked to the required solubilizing groups.

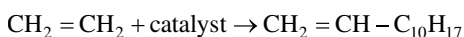
3.3.3 Olefins

Olefins with the desired chain length are prepared by building up molecules from smaller olefins (oligomerization), by breaking down (cracking) larger molecules, or by direct chemical modification of paraffins of the desired chain length. An important historic example of surfactant-grade olefin production by the oligomerization process is the preparation of tetrapropylene, $C_{12}H_{24}$:



It may be prepared by the oligomerization of propylene, a by-product of refinery operations, under the influence of a phosphoric acid catalyst. The reaction conditions are drastic, and extensive random reorganization of the product molecules occurs with substantial formation of intermediate isomers in the C₁₀–C₁₄ range. The final product is composed of a variety of highly branched isomers and homologues, with the double bond usually situated internally in the molecule.

A second type of built-up olefin becoming more common is that obtained by the polymerization of ethylene using a Ziegler–Natta catalyst. Such materials are predominantly linear with even carbon numbers, although branched isomers are present in small amounts. The ethylene raw material historically has been more expensive than propylene. The catalyst is also more expensive and the reaction conditions more sensitive and critical than those for propylene oligomerization. For example, under the right conditions the process can produce a product mix composed predominantly of the α -olefin C₁₂H₂₄:

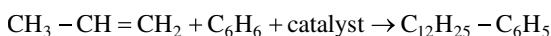


Production of detergent-class olefins from higher molecular weight precursors is accomplished by the cracking process, which uses high temperatures to split high molecular weight paraffins into smaller units. A catalyst may also be employed in the process. Basically, the reaction involves the splitting of a paraffin into two smaller molecules, a paraffin and an olefin. In practice, a wide range of products is obtained because the original molecules may split at any spot along the chain and the resulting products may themselves be cracked further. Each olefin molecule that undergoes such secondary cracking produces two more olefins, so the paraffin content becomes progressively smaller. The olefins produced are predominantly α -olefins, with the double bond located at the terminus of the molecule. If the original cracking stock is linear, the product olefins will be predominantly linear; if branched or cyclic structures were originally present, such structures will also appear in the product.

The third route to detergent olefins is from paraffins of the same chain length. In principle, it is necessary only to remove two hydrogen atoms from an adjacent pair of carbons along the chain to produce the desired olefin, but the difficulties of dehydrogenation are such that a two-step process of chlorination and dehydrochlorination has been developed. In either process the reaction easily proceeds past the desired stage to give polychlorinated paraffins and polyolefins, all undesirable by-products.

3.3.4 Alkylbenzenes

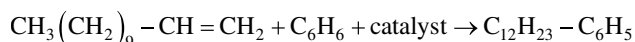
Alkylbenzenes made their first appearance as hydrophobic groups in the late 1940s as a result of new industrial processing capabilities related to the chemistry and chemical engineering of aromatic alkylation reactions. They were prepared by the more or less random chlorination of kerosene and the subsequent Friedel–Crafts alkylation of benzene, denoted here as C₆H₆. Their real dominance in the field began in the early 1950s with the appearance of tetrapropylene-based alkylbenzenes, a better and cheaper product obtained in a one-step process involving addition of benzene across the double bond of the olefin. A variety of Friedel–Crafts catalysts may be employed including aluminum chloride or hydrogen fluoride:



The alkyl group of the alkylbenzene might be expected to have a carbon backbone identical to that of the olefin from which it was derived. This is true in most, but not all, cases because the

alkylation process may cause rearrangement of the carbons in the chain. Furthermore, the reaction of the benzene ring with the double bond of the olefin involves a number of intermediate steps during which isomerization may occur, so that the benzene may finally link on at some position other than that of the original double bond. Thus, each of the many species that make up the olefin feedstock may give rise to several isomeric alkylbenzenes, and the resulting material is an even more complex mixture than the original. Gas chromatographic analysis of typical products may show more than 100 at least partially resolved components.

Propylene-derived alkylbenzenes were pretty much phased out in the 1960s because of their exceptional (and undesirable) biological stability and were replaced by the linear alkylbenzenes prepared from linear olefins or intermediate chlorinated paraffins. These products, like the tetrapropylene (TP), have a chain length that may range from C₈ to C₁₆, variously distributed according to the specific preparation procedure and the properties desired in the final surfactant. The nominal carbon values for most commercial products are C₈ and C₉ alkyl groups:

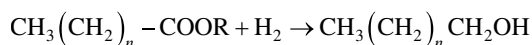


Alkylation of benzene with a linear olefin commonly results in a mixture of all possible linear secondary alkylbenzenes with that total carbon number, even though the original olefin may have been a pure compound. During the alkylation reaction a rearrangement occurs so that the ring bonds at any of the carbon atoms along the chain except the ends. Primary alkylbenzenes are not formed in this process. At equilibrium, the same isomers will be formed regardless of the original location of the double bond. Indeed, any of the five dodecylbenzene isomers can be converted into a mixture of all five by treatment with AlCl₃, the catalyst often used in the alkylation. A similar mixture is obtained using the chloroparaffin process. Since there is not much difference in the reactivity of the 26 hydrogen atoms in dodecane, all possible monochloroisomers are present in the chlorododecane, and all possible phenyl isomers may be present in the resulting dodecylbenzene mixture, including a small amount of the primary isomer.

3.3.5 Alcohols

Long-chain alcohols have been used as a source of detergent hydrophobes since the earliest days of synthetic detergent manufacture. Linear alcohols have been used since the beginning, branched alcohols being a more recent addition to the chemical arsenal.

The classical route to a linear alcohol is by the reduction of the carboxyl group of a natural fatty acid. Actually, an ester of the carboxylic acid is usually employed, since the carboxyl group itself reacts rather sluggishly. Lauryl and tallow alcohols are two of the most commonly used substrates for surfactant synthesis. The first is derived from lauric acid, predominantly a C₁₂ acid but also usually containing some amounts of lower and higher homologues. The tallow alcohols average around C₁₈. Depending upon the reduction process used, they may contain some unsaturated alcohols derived from the unsaturated acids in the original fatty acids:



Since the early 1960s linear primary alcohols have been available from petroleum sources, namely, ethylene. The process for their preparation is similar to the Ziegler process for linear olefins, except that the last step is an oxidative one yielding the alcohol instead of an olefin. Like oligomers of ethylene, the Ziegler-derived alcohols are produced in even-numbered chain lengths. The average chain length and distribution of homologues can be controlled somewhat by the

reaction conditions and completely by subsequent distillation. The —OH groups are at the end of the chain, so that they are identical with the alcohols derived from the natural fatty acids. However, the two products may differ slightly because the amounts and distribution of minor products and impurities may differ.

Branched-chain alcohols were used extensively for surfactant manufacture prior to the changeover to the more readily biodegradable linear products. They were usually derived from polypropylenes by the oxo process, which involves catalytic addition of carbon monoxide and hydrogen to the double bond in a sequence of reactions. Thus, the tetrapropylene derivative is nominally a C₁₃ alcohol, as highly branched as the original raw material.

If a linear α -olefin is used in the oxo process, addition may occur at either end of the double bond to give a mixture of linear primary and methyl branched secondary alcohols. Substitution further down the chain occurs only in small amounts, and with the proper choice of reaction conditions, the proportion of linear primary alcohol may reach 80% or more.

The development of linear paraffin supplies for the production of linear alkyl sulfates (LAS) also made many secondary alcohols feasible as surfactant hydrophobes. Here the —OH group may be introduced by reaction of the paraffin with oxygen, or by chlorination and subsequent hydrolysis. In either case all possible isomers are formed, and the OH group is found on any of the carbons along the chain.

3.3.6 Alkylphenols

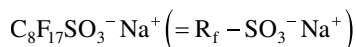
The alkylphenol hydrophobes are produced by addition of phenol to the double bond of an olefin. The alkyl group may be linked to the ring either ortho, meta, or para to the hydroxyl group, and the position can have a significant impact on the characteristics of the resulting surfactant. The earlier commercial products were derived from branched olefins such as octyl phenols from diisobutylene and nonylphenols from tripropylene. More recently, linear alkylphenols have become available with the development of linear olefins for LAS.

3.3.7 Polyoxypropylene

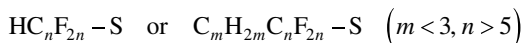
The polyoxypropylene (PO), oligomers of propylene oxide, can be cited as an example of non-hydrocarbon hydrophobes since they contain numerous oxygen atoms in the chain. A complete line of surfactants known commercially as the “plurionics” (among other commercial names) has been developed and has found applications in many areas. These are block copolymers of propylene oxide and ethylene oxide. By careful control of the relative amounts of each component incorporated into the polymer, it is possible to exercise a subtle control over the solubility and surfactant character of the product. The character of other hydrophobes such as alcohols and alkylphenols may also be modified by addition of propylene oxide.

3.3.8 Fluorocarbons

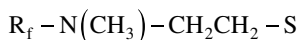
An important addition to the spectrum of available hydrophobic functionalities for the design of surfactants is that in which fluorine is substituted for hydrogen on the carbon chain. Substitution may be complete to produce the “perfluoro” materials (R_f) such as sodium heptadecafluoro octane sulfonate:



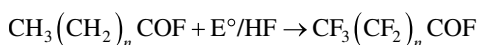
or they may possess a terminal hydrogen (HR_f) or short chain alkyl group with the general structure:



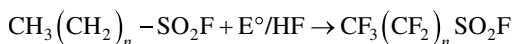
where S may be any of the solubilizing groups discussed. Hydrocarbon groups may also be encountered associated with linking functionalities such as:



The most commonly encountered commercial fluorosurfactant hydrophobic groups are produced by the electrolytic fluorination of the corresponding alkyl carboxylic acid fluoride or sulfonyl fluoride:



or

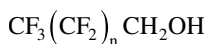


The fluorinated products may then be hydrolyzed to the corresponding acid and neutralized or functionalized by reaction of the reactive acid fluoride to introduce linking groups such as the sodium 2-sulfonamidoethane sulfonate:



Although normal straight-chain hydrocarbon starting materials may be used in the electrolytic process, some branching will always result, commonly yielding materials with up to 30% branched isomers.

Perfluorinated or fully fluorinated alcohols cannot be prepared directly from the electrolytic process since they require the reduction of the corresponding carboxylic acid to yield structures like



The presence of the two hydrogens alpha to the hydroxyl is synthetically useful, however, because the perfluorinated alcohols cannot be effectively used in esterification reactions – the perfluorinated products, when obtained at all, are very unstable to hydrolysis.

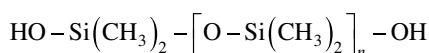
Hydrogen-terminated fluoroalcohols can be produced by the oligomerization of tetrafluoroethylene. In such a reaction, the product will be a mixture of homologous alcohols with an average molecular weight similar to those obtained in the preparation of POE-containing materials. It is also possible to obtain perfluorinated materials in the oligomerization process.

As a class, fluorocarbon compounds in which all carbon–hydrogen bonds have been replaced by carbon–fluorine produce some of the lowest surface tensions and surface energies of any substances currently known to science. If surface activity is defined as the tendency of a substance to reduce the total free energy of a system by preferential adsorption at available surfaces and interfaces, or aggregation to form micelles, the fluorocarbon surfactants can also be considered to be some of the most surface-active materials around. In addition, the electronic nature of the carbon–fluorine bond is such as to make them the most chemically stable of surfactants, able to withstand temperatures and chemical environments that would quickly destroy conventional hydrocarbon-based materials.

As a result of those characteristics, the fluorocarbons are rapidly finding application in many technological areas in which hydrocarbons are either much less effective or chemically incompatible. Unfortunately, the wide use of fluorocarbon surfactants is limited by their relatively high cost, their environmental persistence, and the persistence and possible detrimental health effects of intermediates in their production. In some situations, however, their superior surface activity is essential and outweighs other factors.

3.3.9 Silicone-Based Surfactants

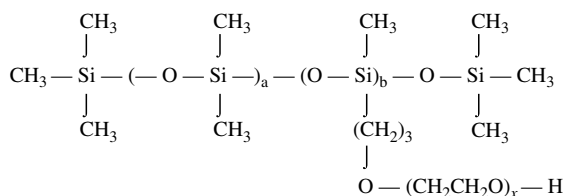
Another type of non-hydrocarbon-based hydrophobic group gaining importance in the field of surfactant technology is that in which siloxane oligomers, primarily dimethyl siloxanes,



can be functionalized to produce water-soluble or water dispersible materials as well as materials well suited to preparing water-in-oil emulsions and dispersions (Figure 3.2). Although the siloxane hydrophobic groups are really oligomeric or polymeric, they are being addressed here instead of in Chapter 9 simply as a matter of context related to the introduction of different surfactant families. They will be mentioned again in Chapters 9 and 13.

Surface-active materials having dimethyl siloxane and similar hydrophobic groups, sometimes with longer alkyl chains or other substitutions, usually exhibit surface activities falling somewhere between those of the normal hydrocarbons and the perfluorinated compounds discussed above, although some match or even exceed those of the fluorocarbons. Because of the nature of the siloxane linkage, such surfactants do not always follow the usual rules of surfactant activity with regard

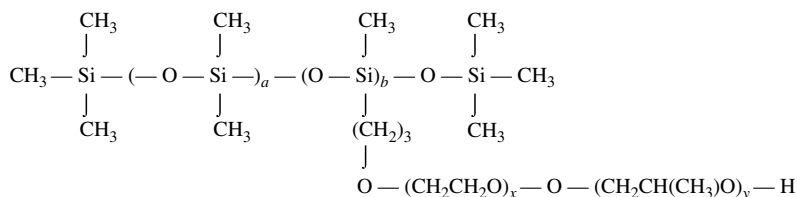
(1) Hydroxyl-terminated (POE) dimethicone copolymers



(a) = a silicone polymer (dimethicone), (b) = a functionalized dimethicone copolymer,

(x) = a hydroxyl-terminated POE polymer

(2) Hydroxyl-terminated copolymer (POE-POP) dimethicone copolymers



(x) = a POE polymer, (y) = a hydroxyl-terminated POP polymer

Figure 3.2 Chemical structures of basic silicon-based surfactants.

to such things as micelle formation and solubilization. They are very effective at the liquid–air interface, even in many nonaqueous solvents, and find wide application as antifoaming agents (see Chapter 11). Extensive experimental data are just becoming available on the siloxane surfactants, possibly because of difficulties characterizing the siloxane group and because much of the work in the area is of a proprietary nature.

The term “silicones” is used for a wide variety of chemical products that are used in many different technical application areas. Silicone-based surfactants have received attention due to their powerful surface tension reduction and wetting properties. A number have been found useful as additives for paints and coatings, as discussed in Chapter 13, but perhaps their strongest area of application is in household and personal care products because they have a relatively low coefficients of friction and do not produce abrasion when in contact with the human skin. They also have found success in polyurethane foams, friction reduction, etc.

All silicone additives for coatings are based on the relatively simple chemical structure of the polydimethylsiloxanes. The backbone consists of several Si—O— units (siloxane units), where each silicon atom carries two methyl groups. One way to modify this structure is to vary the chain length and thus the molecular weight. Higher molecular weight means reduced solubility in coating systems and lower compatibility. Products with a very high molecular weight are so incompatible and insoluble in most coating systems, and that they create craters in a very defined and reproducible way and therefore can only be used for special effect coatings and finishes.

In order to modify the properties of the poly-siloxanes, it is possible to replace the methyl groups (partly) by other side chains. The resulting products are usually termed “organically modified” poly-siloxanes. This organic modification is a good way to control the compatibility of these structures with various continuous liquid phases and in particular with coating systems. The organic side chains improve the compatibility of the materials with surrounding solvents and polymers. Such an approach helps avoid some of the problems usually associated with molecular weight. In most cases, the poly-siloxanes are modified with polyether chains based on polyoxyethylene (POE) and polyoxypropylene (POP) chains.

Like the “pluronic” POE-POP polymeric surfactants discussed in Chapter 9, this method of molecular modification offers many possibilities for the synthesis of silicone-based additives with very specific surfactant property profiles, essentially tailor-made to meet the specific requirements of many areas of application. The dimethyl groups are responsible for a low surface tension of the silicone additives, and variation of the ratio of dimethyl groups to polyether modifications ($x : y$) therefore offers an ideal way to adjust the surface tension to specific values. There still is the additional possibility to influence the surface tension by replacing some of the remaining dimethyl structures by larger alkyl groups. This generally increases the surface tension of the silicone product and reduces the surface tension reduction effect of the additive.

In addition, the structure of the polyether chain itself can be modified. These polyethers basically are built up from ethylene oxide (EO) and propylene oxide (PO) units. Polyethylene oxide is, of course, quite hydrophilic, whereas polypropylene oxide is more hydrophobic. The EO/PO ratio, therefore, controls the overall polarity of the silicone additive: high EO amounts increase the polarity, and the additive becomes more compatible in polar coating systems, and the additive even may become water soluble. However, at the same time also, its tendency of foam stabilization increases. High PO amounts on the other hand reduce water solubility and increase defoaming properties.

As indicated above, by adjusting the polarity of the non-silicone chain, it is possible to synthesize silicone additives that are compatible with aqueous coating systems. However, it is sometimes observed that the efficiency of such additives is not optimal, especially when wetting of low surface

energy substrates such as a hydrophobic polymer is concerned. As is to be expected, the water content in such systems results in a relatively high surface tension, higher than in solvent-based coatings. Such a liquid surface tension–solid surface energy mismatch will often produce potential coating problems (see Chapter 13). For such cases, the fluorocarbon and silicone surfactants present viable choices for possible solutions. As discussed for the fluorocarbon materials above, the silicones can be chemically modified in many ways to produce, hopefully, a solution for all situations – a really tall order in our complex world. Chemically these additives also are polyether-modified siloxanes, but their molecular weight is much lower, resulting in a pronounced surfactant-like structure. Due to this structure these additives strongly reduce the surface tension in aqueous systems; they are nearly as active as fluorocarbon surfactants. Compared with the fluorocarbon surfactants, the silicone surfactants, however, have one important advantage: foam stabilization by silicone surfactants is nearly absent, whereas fluorocarbon surfactants can cause problems in this respect.

3.3.10 Nonchemically Produced, a.k.a. “Natural” Surfactants

Having introduced a general view of the different molecular structures that can be used to produce useful synthetic surface-active materials, one other relatively new class of surfactants has been gaining interest in many areas of surfactant applications. That class is what are often referred to as “natural” surfactants or “biosurfactants.” Those materials are isolated from plants or the fermentation of bacteria, fungi, yeasts, etc. Because of their biological origin, they quite often do not fit into the chemical categories described above. In particular, the natures of their hydrophobic and hydrophilic groups are often much more complicated than the simple synthetic materials above, and as a result, they do not lend themselves to direct manufacture starting from the simple raw materials used in conventional surfactant production processes such as oleochemicals or petroleum feedstocks. Because of their different lineage, so to speak, they will be discussed separately in Chapter 4.

4

Natural Surfactants and Biosurfactants

Over the last few decades, an important part of the world's population has demonstrated not only significant concern about the increasing use of “synthetic” chemical products such as surfactants, and the accompanying consumption of petroleum and other “nonrenewable” raw materials sources, but also with respect to possible or imagined threats to human health and the environment in general. This ever-increasing environmental concern about surfactants, as well as more practical aspects directly related to surface activity, has triggered an interest in “natural” surfactants, especially in applications related to personal care products, pharmaceuticals, and other applications with direct potential effects on the environment, which ultimately covers just about everything. In addition to the “eco-friendly” points of view about synthetic surfactants, there are those of the basic “natural-is-better” movement that expounds the supposed greater safety and effectiveness of natural materials. There are four basic categories of surfactants, excluding those prepared using strictly petroleum-derived raw materials such as many of those discussed in Chapter 3, that might be called natural in terms of the relative importance of the raw materials used in their preparation. These types of surfactants include (i) surfactants containing naturally occurring hydrophobic groups, usually fatty acids or fatty alcohols, making up a significant percentage of all surfactants; (ii) those prepared using natural hydrophilic group such as sugars, natural polyols, amino acids and peptides, etc.; (iii) those composed of naturally derived polar head groups and hydrophobic tails that must be joined together “synthetically” to produce the surface-active molecule; and (iv) those isolated in tact from living organisms such as yeast, fungal, or bacterial fermentation and a number of plant sources, completely synthesized by natural processes. The latter group of natural surfactants is usually referred to as “biosurfactants” and will be emphasized in this chapter. The first three groups are covered in general in Chapter 3 and will only be mentioned briefly here. Groups 1–3 are referred to as natural in some contexts, although they are most often classed among the usual synthetic surfactants.

In this chapter, emphasis is placed on what one could call the “true” natural surfactants or biosurfactants. The ones are, in fact, synthesized naturally by living organisms and isolated as such. The biosurfactants have a completely different genealogy from the others and are the real examples of natural surfactants. The information presented will be mostly “narrative” in the sense that specific technical data will be limited to a few examples of chemical structures and comments about some specific functional characteristics. Most of the chapter will be concerned with general information about sources, general characteristics, possible applications, possible advantages and disadvantages relative to synthetic materials, and some ideas about the future development of these materials.

4.1 What Makes a Surfactant “Natural”?

The term “natural surfactant” is not unambiguous. It can mean different things to different people depending on their areas of scientific or commercial interest or even philosophical persuasion. Strictly speaking, from a linguistic point of view, a natural surfactant should be one obtained in tact directly from a natural source. To meet the strict linguistic standard, the source may be of plant, animal, microbial, fungal, or yeast origin and should be isolated or purified using procedures such as solvent extraction, filtration, precipitation, distillation, or some other physical technique. The process should not involve any kind of synthetic modification during the separation process or as a post-isolation treatment. There are not a great many currently available commercial surfactants that can meet those high standards.

Lecithin, one the oldest and best examples of what may be called a truly natural, commercially produced surfactant, is widely used in foods, cosmetics, and other personal care products. It is not only obtained commercially primarily from soybean oil processing but is also found in smaller quantities in corn and other grains and in egg yolk. That found in corn and other grains is present in such small quantities that its isolation for commercialization is not economically feasible and it is usually reincorporated into animal feed by-products of grain processing. That derived from egg yolk, while being present in significant quantity, is far too expensive to be sold as a commercial surfactant.

The industrial process for the isolation and purification of lecithin is a relatively straightforward and well-established, if a little messy, chemical process. It is a natural by-product of the production of refined soy bean oil. The industrial processing of lecithin is described in a little more detail in Chapter 13. For other truly natural surfactants, however, the costs of production, isolation, and purification can be very high relative to the synthesis of “nonnatural” alternatives. Most such products are present in the natural sources in small quantities, and their isolation tends to involve laborious and low yield processes. In most cases, the processing costs will be much higher than those of producing an equivalent synthetic product. It will take time for the unfavorable economics between the two classes of materials to change unless or until new, much more efficient processes are developed that yield biological-based surfactants in much higher yields. One example of such a possibility would be the development of new fermentation processes and isolation and purification technology. Those points will be discussed more detail in Section 4.3. Of course, such new bio-processes will probably involve the use of genetically modified strains of yeasts, fungi, and bacteria, which, for some people, could call into question the use of the word “natural” in conjunction with such products. Such is the world we live in.

Natural surface-active compounds can be found in relative abundance in both plant and animal systems, so they cannot be considered scarce, as such. Saponins, for example, are a class of naturally occurring amphiphilic compounds found in particular abundance in various plant species, as well as a few marine organisms such as the sea cucumber. They have been known and used for centuries, although until the development of modern chemical identification techniques the users had no idea what they actually were. They are amphiphilic glycosides originally characterized by the soap-like foam they produce when shaken in aqueous solutions. Structurally, they have one or more hydrophilic glycoside groups combined with a hydrophobic triterpene ring (Figure 4.1a). Such species are abundant, and many have been identified and characterized by the biological community, usually being referred to simply as polar lipids or some derivative term. In biological systems, those natural surfactants fulfill essentially the same functions as those in nonbiological or technical applications. Those functions include emulsification and, in some instances, demulsification, surface modification (wetting agents), dispersion stabilization, solubilization, transport, etc.

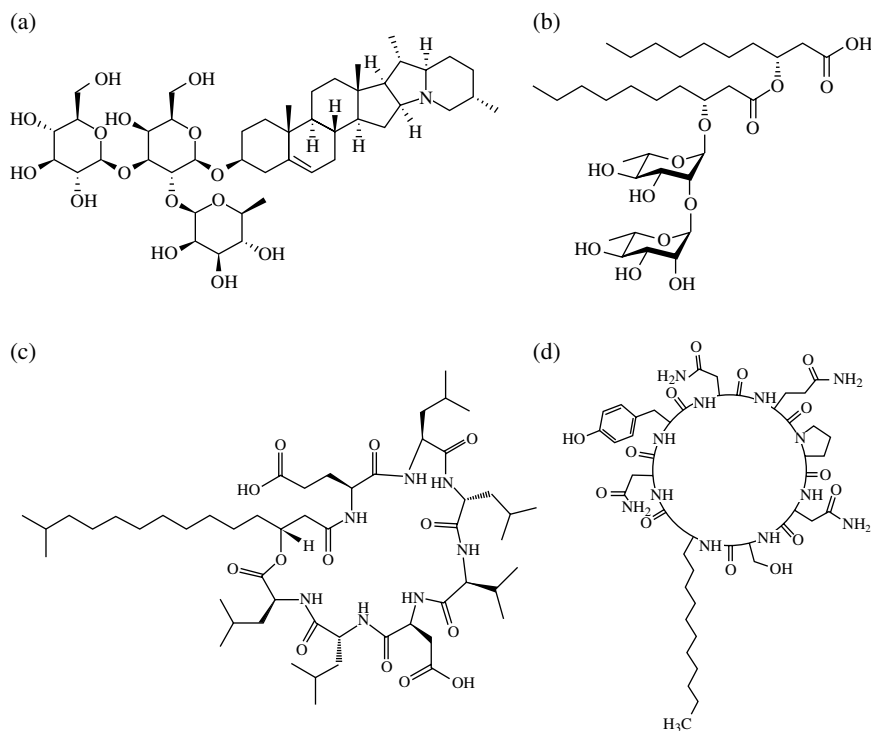


Figure 4.1 Structures of some known biosurfactants.

As opposed to the very restricted definition of “natural” surfactants, the term is now sometimes used in a much more liberal sense. In general usage, to take advantage of the magic word “natural,” surfactants synthesized using natural raw materials are quite often referred to as being natural. Materials fitting that expanded definition would include fatty acid esters of sugars, glycerol, polyglycerols and other polyols, and esters and amides of natural amino acids. It should be kept in mind that when the word “sugars” is used in the context of natural surfactants, it includes a number of compounds beyond the everyday sugars such as glucose, sucrose, lactose, etc. In some cases, it may be enough to label a product as natural if only one of the components of the molecule, either the hydrophilic head group or the hydrophobic tail, is obtained from a truly natural source. As examples, a natural sugar ester in which the hydrophilic group is a natural sugar, but the hydrophobic group is a nonnatural fatty alcohol, might be termed natural. It is important to keep in mind that so-called natural fatty alcohols are prepared by a process of esterification, usually with methanol – “methanolysis” if the starting material is triglyceride – followed by catalytic reduction of the methyl ester. Alternatively, a natural fatty acid may be esterified with a synthetically prepared or modified hydrophile. The widely used sorbitan esters would be a good example of such surfactants. Although sorbitol is a natural sugar in the sense that it is found in nature, the sorbitol used in the synthesis of sorbitan esters does not come from one of the natural sources. Industrial sorbitol is mainly produced by the enzymatic reduction of glucose or corn syrup reducing sugars having a terminal aldehyde to a terminal alcohol producing sorbitol. Some of those almost-natural surfactant classes will be briefly described below.

4.2 Surfactants Based on a Natural Sugar-Based Polar Head Groups

Various types of sugars or polyols derived from sugar are used as surfactant polar head groups. Representative structures of the four surfactant types are shown in Figure 4.2. Sorbitan esters (Figure 4.2a) and ethoxylated sorbitan esters, well known under the trade names of Spans, Tweens, or Polysorbates, have been around for many years. Some of them are discussed in more detail in other chapters (see Chapter 13). In recent years there has been a focus on three newer classes of surfactants with sugar or a sugar-derived polyol as hydrophilic head groups: sucrose esters (Figure 4.2b), alkyl glucamides (Figure 4.2c), and alkyl polyglucosides (Figure 4.2d).

Fatty acid esters of sucrose (Figure 4.2b) have been investigated for a number of years and have carved out a significant niche in various applications, but especially those related to foods and beverages. While the raw materials for their synthesis are readily available and not particularly costly, the thermal sensitivity, and solubility characteristics of sucrose make a simple, straightforward synthetic pathway unavailable for the production of high purity products. The processes available at an industrial level require the use of expensive solvent systems such as dimethylformamide (DMF) or dimethyl sulfoxide (DMSO). Not only are those solvents expensive and somewhat dangerous, but also they are tightly regulated and very limited in terms of their presence in products for human consumption. That means that extreme purification

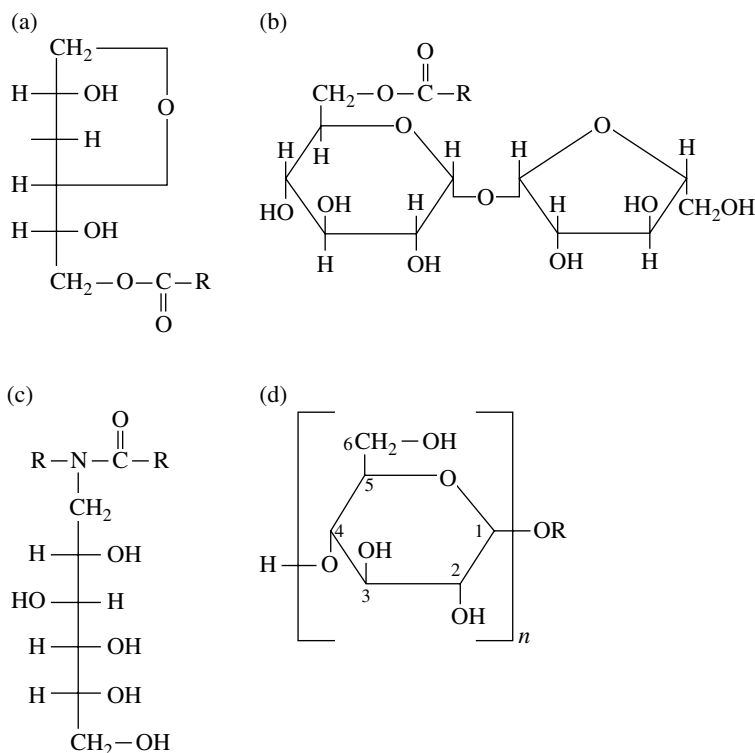


Figure 4.2 Representative structures of sugar-based fatty acid ester of (a) sorbitan, (b) sucrose, (c) acyl glucamides, and (d) polyglucosides.

techniques are required before the sucrose ester products can be used in most applications. Nevertheless, sucrose esters have reached a significant market in uses where the added cost is justified in the final product. The sucrose ester surfactants have been investigated and commented on in several chapters.

Alkyl glucamides (Figure 4.2c) are commercially important products. The surfactant used in large quantities for the detergent sector is the C₁₂-derivative *N*-dodecanoyl-*N*-methylglucamine. The surfactant is prepared from glucose, methyl amine, hydrogen, and methyl laurate by a two-step reaction. Alkyl glucamides have been the subject investigations for a number of years, and several comprehensive reviews have been published.

There is currently a strong interest in exploring alkyl polyglucosides (Figure 4.2d) as surfactants for use in several types of applications. They can be synthesized by direct reaction of glucose with a fatty alcohol, using a large excess of alcohol to minimize sugar oligomerization. Alternatively, they can be made by *trans*-acetalization of a short-chain alkyl glucoside, such as ethyl or butyl glucoside, with a long-chain alcohol. An acid catalyst is used in both processes. Either glucose or a degraded starch fraction can be used as starting material. Alkyl polyglucosides can also be made by enzymatic synthesis using β -glucosidase as catalyst. There are considerable differences between the mixture obtained by organic synthesis and the pure enantiomers obtained by the bioorganic route. Polyglucosides are stable at high pH and sensitive to low pH where they hydrolyze to the sugar and fatty alcohol.

Since a sugar hydrophilic group tends to be more water soluble and less soluble in hydrocarbons than an equivalent polyoxyethylene unit, alkyl polyglucosides, and other polyol-based surfactants are more lipophobic than polyoxyethylene-based surfactants. This makes the surface activity of alkyl polyglucosides at oil–water interfaces different from that of conventional non-ionic materials. In addition, polyglucosides do not exhibit the inverse solubility vs. temperature relationship that normal nonionics do, that is, they do not have a cloud point. This makes an important difference in the solution behavior of alkyl polyglucosides compared with polyoxyethylene-based surfactants. An important reason for interest in alkyl polyglucosides, aside from their interesting surfactant properties, arises from their favorable eco-friendly profile: they have a high rate of biodegradation in standard tests and show low aquatic toxicity. Polyglucosides exhibit good dermatological properties, being very mild to skin and eyes making them attractive for personal care products. Alkyl polyglucosides are also finding more applications in a variety of technical applications.

Alkyl polyglucosides, both those prepared by organic synthesis and those from enzymatic synthesis, have been shown to exhibit aqueous solution behavior equivalent to or better than their POE counterparts. The micellar phase region is usually large, moving into a pattern of liquid crystalline phases at higher concentrations. It has been observed that some polyglucoside surfactants show a rather sharp gap in the micellar region that is postulated to result from a transition from normal micelles with aggregation numbers in the 200–400 range at lower concentrations, to larger aggregates, possibly “branched,” aggregated or flocculated micelles that form a network through entanglement. The polyglucosides also exhibit other interesting behaviors related to their mesophases and mixed micelle formation. Some of those points will be discussed in Chapters 6 and 7. The majority of work on glycoside surfactants has been made on alkyl glucosides, but more work is now dedicated to other sugar hydrophiles, one being the alkyl maltosides. The results obtained with the maltoside surfactants generally follow those found for the APGs with the same hydrophobic chain. Many of the “unusual” characteristics of maltosides agree very well with those previously obtained with polyglucosides of the same alkyl chain length, although firm explanations for some of those oddities are still lacking.

4.3 Biosurfactants

In the realm of what might be called “true” natural surfactants, new classes of biosurfactants isolated from plant and microorganism sources are becoming of increasing scientific and industrial interest. Biosurfactants are usually extracellular amphiphilic compounds. They are produced by a variety of microorganisms using various substances as carbon sources, including potentially dangerous waste materials. There is increasing interest on this topic because of their unique properties such as usually low toxicity, functionality under extreme conditions, extensive “recycling” potential using renewable substrates, and a rapid biologically degradable nature. The diversity of these molecules supports their potential application in the field of petroleum, medicine, agriculture, food, cosmetics, etc. They are also sometimes promoted as being potentially effective in curtailing the greenhouse effect by reducing emissions of CO₂ that result from traditional synthetic processes, although that aspect is speculative at the moment. They can, however, be termed “green” because of their generally low toxicity, high level of biodegradability, and relative stability under a broad range of environmental conditions.

Despite offering a wide range of diverse chemical structures and, in many cases, exhibiting better interfacial properties than many synthetic chemical surfactants, biosurfactants are not yet in a position to compete extensively with their synthetic counterparts because of their high production and downstream costs. The commercial realization of these eco-friendly biomolecules is restricted by low productivity, expensive downstream processing, and lack of appropriate understanding of the bioreactor systems for their production. But it is to be expected that in the future better reactor design and product isolation and purification technology would be developed and perhaps strains of “over producing” organisms – ones that produce the desired compound at levels significantly higher than the “native” strains – will be developed. When some or all of those goals are reached, production costs will decrease, and yields will increase. At that time, biosurfactant production may be both ecologically and economically favored. The information presented here is just a brief overview of some of our present understanding of biosurfactants, their properties, some possible advantages and disadvantages, production capabilities, their characterization, possibly advantageous areas for their application, and some speculation about future areas of research.

4.3.1 Biosurfactants as Nature Makes Them

For some time, it has been known to science, mostly that related to biological systems, that some microorganisms produce both high and low molecular weight surface-active compounds naturally. Those compounds have been found to help carry out important functions in the organisms producing them, otherwise why would they waste vital resources and energy synthesizing them? Modern preoccupations with the use of “nonrenewable” resources such as petroleum, ecological concerns with environmental contamination and CO₂ production, the supposed advantages to human health of the use of “natural” instead of “synthetic” materials in our daily lives, and the like, have prompted increasing research investigating the physicochemical properties of such materials, their possible environmental and health impacts, and the development of technical processes applicable to their commercially viable production, purification, and use.

Biosurfactants are synthesized by living cells and exhibit the characteristic interfacial properties common to all surfactants: the lowering of surface and interfacial tensions, emulsification and dispersion preparation, solubilization, foaming, wetting, detergency, and antimicrobial activity in some cases, etc. Most biosurfactants are “exolipids,” meaning that they are produced and

function outside the actual cell walls of the producing organism, although they may be cell bound in some cases. Their exolipids character simplifies somewhat the processes related to isolation and purification.

Many of the more interesting new classes of biosurfactants are produced by yeasts, bacteria, or fungi from various “food” substrates including animal and vegetable fats and oils, sugars and carbohydrates, hydrocarbons, especially straight chain alkanes, and various classes of industrial and household wastes. Based on those advantages, they seem to present a potentially useful means of recycling a number of undesirable “garbage” items left over from the day to day activities of the human species. As an example, *Pseudomonas aeruginosa*, a common Gram-negative, rod-shaped bacterium that can cause disease in plants and animals, including humans, is able to decompose hydrocarbons and has been used to break down heavy sludge and tar balls from oil spills. A species of considerable medical importance, *P. aeruginosa* can produce rhamnolipid biosurfactants from a wide range of substrates including C₁₁ and C₁₂ alkanes, common organic acids such as succinate, pyruvate, and citrate; from glycerol; from olive oil and other oleochemicals; from simple sugars including fructose, glucose, and mannitol; and probably many more potentially interesting substrates.

In general, the surfactant characteristics of biosurfactants parallel those of synthetic materials. The measured **cmc**s of biosurfactants have been found to range from 1 to 200 mg/L and their molecular masses from 500 to 1500 Da. One of the first commercial biosurfactants on the market was sophorolipids, but in recent years they have become increasingly interesting as subjects of investigation for the scientific and industrial communities.

4.3.2 Properties of Biosurfactants

Interest in research on the production and application of biosurfactants is increasing due to their apparent environmentally friendly nature and lower toxicity compared with synthetic surfactants. Diverse functional properties such as emulsification, foaming, wetting, cleansing, surface activity, phase separation, and reduction in the viscosity of crude oil make them some of the potentially most versatile new process chemicals in the technological tool kit related to surfactants. Like all surfactants, the activities of biosurfactants depend to a great extent on their critical micelle concentration (**cmc**).

As discussed in Chapter 6, the **cmc** is used as the criteria to indicate surfactant efficiency. More efficient biosurfactants have a lower **cmc**, i.e. less biosurfactant is needed to decrease the surface tension to a given level. The hydrophile–lipophile balance (HLB) of the biosurfactants indicates the relative balance between the hydrophilic and hydrophobic parts the molecule and, in its most common usage, the type of emulsion (e.g. oil-in-water or water-in-oil) it will be most likely to produce. Emulsifiers with low HLB stabilize water-in-oil emulsion, whereas emulsifiers with high HLB are best at stabilizing oil-in-water systems. In general, the surface activity of biosurfactants is similar to that of synthetic surfactants.

Some of the distinctive features of biosurfactants include:

- 1) A good biosurfactant can reduce the surface tension of water from 72 to 35 mN/m and the interfacial tension of water against *n*-hexadecane from $40 \geq 1$ mN/m.
- 2) In general, biosurfactants tend to be very efficient surfactants, and their **cmc** values are about 10–40 times lower than that of comparable chemically synthesized surfactants.
- 3) Biosurfactants are generally excellent emulsifiers, some producing emulsions that are stable for months and even years.

- 4) Although good emulsifiers, some biosurfactants also exhibit the ability to destabilize emulsions under some conditions, which is an important attribute in applications such as oil recovery, since an emulsion is useful for the extraction of crude oil but must be broken once it is recovered from the ground and ready for refinery processing.
- 5) Since they are biological “by-products,” biosurfactants in general appear to be more easily biodegraded than their synthetic counterparts. That characteristic obviously makes them appealing on ecological grounds. Tests have shown that some biosurfactants begin to biodegrade immediately when exposed to standard, carefully controlled test conditions, usually being completely degraded within 10 days, while synthetic surfactants generally exhibit a delay of one to three weeks before they begin to break down under identical conditions. In addition, biosurfactants exhibit biodegradation under both aerobic and anaerobic conditions (not at the same rate, however) while the synthetic materials generally show no degradation under anaerobic conditions.
- 6) Some biosurfactants of interest are synthesized by organisms that thrive at high temperatures and pressures, and the resulting surfactant molecules appear to “inherit” that thermal stability. They also seem to survive more extreme pH and electrolyte contents than some synthetic materials.
- 7) Biosurfactants exhibit a relatively wide diversity in terms of the chemical structures available and the surface-active properties available for specific potential applications.

Based on the above general characteristics, biosurfactants can be said to have several potential advantages over synthetic materials, assuming they can be produced in the industrial quantities required. Those potential advantages include:

- 1) The apparent advantage in terms of biodegradability shown by biosurfactants gives them a significant advantage in terms of their ecological impact.
- 2) Synthetic surfactants usually have hydrophobic chains containing 12–18 (or more) carbon atoms plus some branching, all of which tend to slow down biodegradation processes. Many biosurfactants have shorter chains and therefore biodegrade more rapidly.
- 3) Although biosurfactants usually have very good water solubility, they tend to exhibit lower critical micelle concentrations than equivalent synthetic materials.
- 4) Their biological origin generally results in biosurfactants having lower toxicity and greater biocompatibility than synthetic surfactants. Those characteristics would seem to predict that they will be useful in applications such as cosmetics, pharmaceuticals, food additives, agricultural applications, and other specific uses in which those characteristics may be important.
- 5) If economically viable process details are worked out, biosurfactants can be produced from relatively cheap and abundant raw materials. In fact, it may become feasible to produce biosurfactants using industrial wastes and by-products as raw materials, which would help them provide a double environmental benefit and improve their advantage for economical industrial-level production.
- 6) Since many biosurfactants have been found to be stable under harsh conditions of temperature, pH, high salt concentrations, etc., they will obviously be good candidates for use under such conditions; an example being under the harsh conditions found in many oil and gas-bearing geological formations.
- 7) Biosurfactants usually have hydrophilic groups that are outside the “normal” families of such functionalities (Chapter 3). Those differences may enable the biosurfactants to be used with more specificity in such areas as the detoxification of specific pollutants, in specific cosmetic, pharmaceutical, and food applications, and in the de-emulsification of unwanted industrial emulsions, among others.

- 8) Because they can be produced by organisms that feed on such materials, biosurfactants can be effective in controlling oil spills, industrial effluents and accidental discharges, and for the detoxification and bioremediation of contaminated soil.

As with most things in this world, materials that exhibit excellent characteristics for solving certain problems quite often also carry with them the possibility of accompanying disadvantages. For biosurfactants, some of those potential disadvantages include:

- 1) Although biosurfactants show great promise as ecologically friendly solutions, it has been found that under some circumstances, they can, in fact, have negative environmental impacts. For example, in biomedical applications, it has been found that they can produce unwanted hemolytic activity such as the rupturing of erythrocytes. Though that activity in biosurfactants is generally less than found for synthetic materials such as sodium dodecyl sulfate (SDS), cetyltrimethylammonium bromide (CTAB), etc., it is still a concern. Biosurfactants do not appear to have harmful effects on major organs or to interfere with normal blood functions, but care in their use is called for.
- 2) For the time being at least, the mass production of biosurfactants is relatively expensive. Such a disadvantage may be overcome in the future if they can use industrial and public waste products as raw materials. The environmental advantages of such a system would help significantly in offsetting the higher production costs.
- 3) Since they are produced by living organisms, the purification of biosurfactants, especially for use in foods, cosmetics, and pharmaceutical applications, becomes of utmost importance. Not only could low level contaminants be a potential problem, but also whatever the production process might be, it will almost certainly involve multistep processing of dilute solutions downstream with all of the accompanying complications of waste water disposal.
- 4) Biological fermentation processes seldom have unlimited production capabilities in that the producing organism cannot thrive as many of the products and by-products of the fermentation increase in concentration. Most biological processes, that is, are self-limiting with respect to the synthesis of many natural components of their normal environment. In biosurfactant production, that self-limiting process will likely signify relatively low productivity or low yields of the desired product.
- 5) Adding to the probability of low productivity is the fact that biosurfactants, being highly surface active, tend to produce a significant amount of foam. High foam usually means a diluted reaction system is required and that leads to lower production. If immobilized fermentation systems can be found, that problem may be more easily overcome.

The above lists of the potential advantages and disadvantages of biosurfactants provides food for thought about the economics of pursuing them as practical replacements for many of the synthetic materials that make up the surfactant industry worldwide. Nevertheless, they remain a prime candidate for the much sought-after designation as truly “green” surfactants. Even with their higher costs, the market for these materials is expected to increase approximately 6% annually during the 2017–2021 time period, mostly due to their natural and eco-friendly reputation.

4.3.3 Biosurfactant Classification

Biosurfactants are generally categorized by their chemical structure and microbial origin. Structurally, they are, like their synthetic counterparts, amphiphilic compounds containing a hydrophilic group such as an acid group, alcohol, peptide cations or anions, and mono-, di-, or

polysaccharides and a hydrophobic group composed of saturated or unsaturated hydrocarbon chains, such as fatty acids or fatty alcohols, cyclic triterpene structures, etc. The two surface-activity producing functional groups are joined by ester linkages (including lactones), glycosidic linkage (sugar–sugar and sugar–hydroxy fatty acids), and ether bonds.

The biosurfactants can be broken down into two general groups:

- 1) Low molecular weight surface-active agents characterized by efficiently lowering surface and interfacial tensions. Their structures include glycolipids, lipopeptides, and phospholipids.
- 2) High molecular weight species more effective as emulsifiers including polymeric and particulate (i.e., vesicles) surfactants.

Some examples of important types of biosurfactants and the primary organisms that produce them are presented in Table 4.1. The microorganisms listed represent one of the important organisms found to produce a given biosurfactant, but they are not necessarily unique in doing so. The list is far from complete, of course, but illustrates the variety of chemical structures potentially available and the variety of potential producing organisms to be explored.

4.3.4 Some Aspects of Biosurfactant Production

Many microorganisms, such as bacteria, yeasts, and fungi, produce surface-active agents during their normal growth cycle. For instance, the bacteria *P. aeruginosa* produces rhamnolipids and *Bacillus subtilis* produce surfactin; the yeasts, which are unicellular members of the fungi family, *Torulopsis bombicola* and *Candida petrophilum* produce sophorolipids and peptidolipids, respectively; and the fungi *Candida batistae* and *Candida bombicola* sophorolipids. There are many other examples of such potential biosurfactant sources currently under study.

Table 4.1 Some examples of biosurfactants and their primary producing organisms.

Chemical type	Class name	Typical producing microorganism
Glycolipids	Rhamnolipids	<i>Pseudomonas aeruginosa</i> , <i>Pseudomonas</i> sp.
	Sophorolipids	<i>Torulopsis bombicola</i> , <i>Torulopsis apicola</i>
	Trehalolipids	<i>Rhodococcus erythropolis</i> , <i>Mycobacterium</i>
	Cellobiolipids	<i>Ustilago zaeae</i> , <i>Ustilago maydis</i>
Lipopeptides and lipoproteins	Surfactin	<i>Bacillus subtilis</i>
	Viscosin	<i>Pseudomonas fluorescens</i>
	Peptide–lipid	<i>Bacillus licheniformis</i>
Fatty acids, neutral lipids, and phospholipids	Fatty acids	<i>Corynebacterium lepus</i>
	Neutral lipids	<i>Rhodococcus erythropolis</i>
	Phospholipids	<i>Thiobacillus thiooxidans</i>
Polymeric surfactants	Emulsan	<i>Acinetobacter calcoaceticus</i>
	Biodispersan	<i>Acinetobacter calcoaceticus</i>
	Alasan	<i>Acinetobacter radioresistens</i>
	Liposan	<i>Candida lipolytica</i>

Biosurfactants are produced using a wide variety of substrates as carbon and nitrogen sources. In addition to production by growing cells, resting cell systems are also able to produce biosurfactants. Fungi tend to give higher yields of biosurfactant compared with bacteria. The presence of rigid cell walls in bacteria may be the reason behind the difference. In current production systems, it is the downstream processing that most significantly run up the costs of biosurfactants, accounting for up to 60% of the total production cost. This makes commercial production of biosurfactants quite expensive. However, production of biosurfactants from inexpensive substrates and waste by-products is predicted to help overcome the expensive downstream production costs. Residues from agricultural crop production, fruit processing industries, seed oil processing mills, the coffee processing industry, etc., all of which can become potentially problematic waste products, have been found to be potential substrates for biosurfactant production. Some examples of such convenient sources include:

- 1) **Oleochemical processing wastes and by-products.** Oil wastes from vegetable oil processing and the food industry are being used as substrates for biosurfactant production. Sunflower seed oil and oleic acid have been used for the production of rhamnolipids by *Thermus thermophilus* HB8. Incorporation of these cheaper oils and oil wastes as substrates in the industrial production media might reduce the overall costs of biosurfactant production.
- 2) **By-products from dairy processing.** A major by-product of the cheese industry is the whey, which is an interesting source of nutrients for many of the organisms. For example, a common soft or fresh cheese produces approximately 6 L of whey for each kilogram of cheese produced. The whey from dairy industries is a cheap and durable substrate for biosurfactant fermentation. Using dairy wastes as substrates, the production of sophorolipids in significant concentrations were achieved using a two-stage cultivation process with a variety of the yeast *Cryptococcus curvatus*.
- 3) **By-products from gluten and starch processing.** Waste materials from starch and gluten isolation processes are also inexpensive raw materials and suitable for the production of biosurfactants. The wastes from the potato processing industry are a major source of such potential substrates. These wastes are rich sources of nutrients such as carbon in the form of sugars and starch, nitrogen and sulfur from proteins, minerals, trace elements, and vitamins.
- 4) **By-products from sugar processing.** Molasses is the coproduct of sugar industry generated during sugar manufacturing from either sugar beet or sugarcane and is a rich source of available carbon.
- 5) **Animal fat and other wastes.** The meat processing industry is a very large potential source for tallow and other fatty materials that are too difficult to recover for other commercial uses.
- 6) **By-products of soap and oil-seed processing.** Soap stock is a by-product of the oil-seed processing industry. It can also be used for the production of biosurfactant since it is a good source of carbon.

4.3.5 Some Factors Affecting Biosurfactant Production

Biosurfactant production depends not only on the organisms producing the desired product but also on the optimum conditions for maximizing yield. Important parameters affect not only the potential yield of biosurfactant attainable but also the type of product produced. Some of those factors include:

- 1) **General environmental factors.** To insure a high productivity of biosurfactants, it is always essential to optimize the bioprocess to control factors that may influence the product such as

changes in pH, temperature, aeration, and agitation speed. The effect of pH on the production of biosurfactant can be important, especially if the natural production process causes a pH change due to substrate consumption, reaction by-products, etc. Studies seem to indicate that the optimum pH for the production of many biosurfactants is 8.0, which is the natural pH of sea water.

As in many chemical processes, microbial processes for the production of biosurfactant are highly dependent on temperature and can be adversely affected by relatively small variations. Most of the biosurfactant production reported till now has been performed in the temperature range of 25–30 °C, although some materials seem to do best at higher temperatures. Aeration of the fermenting mash by either direct or forced aeration or aeration by agitation facilitates the incorporation of oxygen into the aqueous phase. They can be significant factors that influence the production of biosurfactant.

- 2) **Nutritional factors.** The type, quality, and quantity of biosurfactant produced are affected and influenced by several nutritional factors. The source of carbon will obviously have a significant role in the growth of the various microorganisms as well as production of biosurfactants. Glycerol, glucose, mannitol, sodium acetate, and ethanol are some of the water-soluble carbon sources, whereas *n*-alkanes and olive oil are water-immiscible substrates. Nitrogen is also important for microbial growth since the syntheses of proteins and enzymes depend on it. Several nitrogen compounds such as yeast extract, ammonium nitrate, ammonium sulfate, urea, peptone, sodium nitrate, meat, and malt extracts have been used for the production of biosurfactants. The carbon/nitrogen (C/N) and carbon/phosphorous (C/P) ratios in the nutrient mix are found to be important to biosurfactant yield. Increased productivity of glycolipid (rhamnolipid), for example, seems to be related to high C/N and C/P (as inorganic phosphorous) ratios. Inorganic salts or metal ions, in low concentrations, are often important cofactors of many enzymes. Therefore, metal ion concentrations play an important role in the production of some biosurfactants.
- 3) **Reaction/fermentation systems.** The proper choice of reaction system can also be important in determining the efficiency of biosynthetic processes. Conventional systems for the cultivation of producer organisms include the classic “shaken flask” approach, which would have to be scaled up to a more commercial scale, stirred batch reactors or fermenters, continuous feed-through systems, and integrated microbial/enzymatic processes have all been tried. One of the potential disadvantages for using a bioreactor is that of excessive foam formation caused by the biosurfactant when the solution is aerated and agitated. For example, high foam formation is worsened by the presence of extracellular proteins, which stabilize the foam. That results in increased production costs.
- 4) **Downstream processing – isolations and purification.** Producing an adequate yield of biosurfactant is only step one in the production of a commercially viable product. It is estimated that in most cases, the so-called “downstream” costs account for as much as 60% (or more) of the cost of obtaining the finished saleable product. Conventional “laboratory” methods for recovery of biosurfactants include acid precipitation, solvent extraction, crystallization, ammonium sulfate precipitation, and centrifugation. While those methods are perfectly adequate for small scale production, commercially profitable production systems will almost certainly require more modern technological methods. Some methods being evaluated for biosurfactant isolation and purification include foam fractionation, ultrafiltration, dialysis, column adsorption-desorption using appropriate resins, and ion exchange chromatography. Other methods will no doubt appear over time.
- 5) **Improvements in producer organism strains, a.k.a. genetic engineering.** Genetic engineering approaches have been successfully applied to improve strain performance in several

cases. The combination of engineering and microbiology will probably be required to obtain production systems giving higher yields and lower costs for biosurfactant production.

- 6) **Fermentation and recovery.** As already alluded to, operating conditions of the fermenter system can significantly affect biosurfactant production. The strict control of fermentation parameters such as pH, temperature, agitation, aeration, and dilution rate, the concentration of metal ions, and the nature of the carbon and nitrogen sources will be vital to the development of a commercially viable production system. The recovery or isolation of biosurfactants depends mainly on their ionic charge (chromatography), solubility (water/organic solvents), and location within the producer organism's structure (intracellular, extracellular, cell bound).
- 7) **Isolation, identification, and purification.** Once an efficient fermentation system for the production of a commercial biosurfactant is designed, the next important steps in production are their isolation from the fermentation media, chemical analysis and identification of the desired product, and its purification to make it suitable for the various proposed industrial uses. Several methods such as ion exchange, adsorption-desorption chromatography, solvent extraction, acid precipitation, diafiltration, centrifugation, etc. are available for their purification. Various solvents such as hexane, chloroform, ethyl acetate, pentane, methanol etc. are used for the purification of biosurfactants. For the complete characterization of biosurfactants, several chromatographic and spectroscopic techniques can be used either individually or in combination. They are thin layer chromatography (TLC), high performance liquid chromatography (HPLC), Fourier transform infrared spectroscopy (FTIR), gas chromatographic mass spectrum (GC-MS), nuclear magnetic resonance (NMR), among others.
- 8) **Estimation of biosurfactant activity.** The surface activity of a biosurfactant can be determined in the usual way by measuring its ability to lower surface and interfacial tensions and hydrophilic-lipophilic balance (HLB). Those evaluations may be carried out in the same way as for synthetic materials as discussed in Chapter 3.
- 9) **Analysis of economic factors of production.** Design and economic evaluation of a process is important before constructing and operating a plant, and this requires combined knowledge from both scientific and engineering disciplines. The overall cost analysis includes the estimation of capital and operating expenditure. Several production models or process simulation software applications have been developed to predict the end costs of production of several important biosurfactants. For example, the unit (per kilogram) cost for the production of approximately 100 million kg of sophorolipid annually from glucose and oleic acid or glucose and high oleic sunflower oil is between US\$2.50 and 3.00/kg. Although that price range makes sophorolipids more expensive than their synthetic counterparts in terms of some applications, its wider application potential may make them more attractive in the surfactant market.

4.4 Biosurfactant Applications

Biosurfactants, given their generally excellent interfacial activity and chemical resistance, are under active investigation for use in numerous applications, especially areas that have special requirements with regard to high temperatures and pressures. Some of those potential applications include:

- a) **Microbial-enhanced oil recovery (MEOR).** MEOR is a potentially powerful technique for extracting crude oil remaining in reservoirs with low permeability or crude oil with high viscosity. In the first case, the unrecovered crude is often located in deposits that are hard to access, and the oil remains trapped in the pores by capillary pressure. Because of their good surface

activity, biosurfactants can minimize the oil–water and oil–rock interfacial tensions, thereby lowering the capillary forces restricting or slowing oil movement in the rock formation. Biosurfactants can also act effectively at the oil–water interface forming emulsions that may have greater mobility. The biosurfactant-stabilized O/W emulsion facilitates the removal of oil along with injected water.

- b) **Soil washing and bioremediation of crude oil-contaminated environments.** Highly hydrophobic contaminants have the ability to bind very tightly with soil particles making them difficult to remove and less accessible for natural biodegradation. Synthetic surfactants can facilitate the removal of the contaminants from the soil, but it often requires large amounts of cleaning agent that can itself become a contamination problem. Biosurfactants like rhamnolipids have been found to be effective at removing such contaminants as polycyclic aromatic hydrocarbons (PAH), and pentachlorophenols from soil with a removal efficiency as high as 80%. Crude oil from different sources exhibit very low water solubility and high adsorption efficiency onto soil particles. Oil-contaminated soil is especially difficult for bioremediation since not only the oil is adsorbed onto the particle surface, but also droplets of oil will wet the particles and function as a binder to form clumps that are difficult to break up and clean. In that situation, it is difficult or impossible to gain access to the oil to allow any significant degree of microbial biodegradation. Biosurfactants, being very efficient at lowering the O/W interfacial tension as well as having low **cmcs**, can not only improve the oil mobility as an emulsion but also increase its bioavailability by solubilizing the hydrocarbon and improving the process of biodegradation. Their somewhat unique abilities to interact with crude oil, and similar contaminants make them very useful for applications in the oil industry and remediation activities, and this is reflected in the market, where a large proportion of commercial biosurfactants are destined for petroleum-related applications.
- c) **Metal contamination remediation.** The presence of soil contaminated with heavy metals represents a very hazardous situation for humans and other life forms in our ecosystem. Due to their exceptionally toxic nature, the presence of even low concentrations of heavy metals in the soils has been found to produce serious health problems. Several biosurfactants have exhibited interesting potential for the removal of heavy metal contaminants, among them being those in the rhamnolipid family. Studies have shown them to be good candidates for heavy metal remediation processes.
- d) **Biomedical applications.** Based on their biological origins, it is not surprising that many biosurfactants are the subject of study for their possible use in pharmaceutical and medicinal applications. For example, many biosurfactants show strong antibacterial, antifungal, and antiviral activity. These surfactants may also act as anti-adhesive agents to pathogens and so they are useful for treating many diseases as well as for postsurgical measures to prevent serious infections and adhesions in the area of the surgery. Rhamnolipid produced by *P. aeruginosa*, mannosylerythritol lipids from *Candida antarctica*, surfactin, Iturin, and fengycin lipopeptides produced by *B. subtilis* and *Bacillus licheniformis* have all exhibited antimicrobial activities. Iturin exhibits significant antifungal activity against the morphology and membrane structure of yeast cells. Mixtures of rhamnolipids obtained from *P. aeruginosa* strains are found to have inhibitory activity against the bacteria *Escherichia coli*, *Serratia marcescens*, *Micrococcus luteus*, *Alcaligenes faecalis*, *Mycobacterium phlei*, and *Staphylococcus epidermidis*, as well as excellent antifungal properties against *Aspergillus niger*, *Penicillium chrysogenum*, *Chaetomium globosum*, *Aureobasidium pullulans*, and the phytopathogenic *Rhizoctonia solani* and *Botrytis*

cinerea. Sophorolipids from *C. bombicola* exhibits viricidal activity against human semen. Other advantages and applications of biosurfactant in medicine are gene delivery, immunomodulation, wound healing, insecticidal, antitumoral activities, etc. Obviously, the future bodes well for the future of biosurfactants, especially if the costs can be made competitive with synthetic materials.

- e) **Agricultural applications.** The use of herbicides and other pesticides in agricultural applications can produce, or are perceived to produce, a number of undesirable effects on the environment and human health. Biosurfactants have also exhibited interesting antimicrobial and insecticidal activity that can possibly be used as a more ecologically friendly way to attack crop protection problems. Because of their biological origins, generally low toxicity, and proven rapid biodegradation, biosurfactants are not expected to produce significant adverse effects on the environment or on human health. Lipopeptide biosurfactants produced by several bacteria show insecticidal activity against fruit fly *Drosophila melanogaster*, and hence they can be used as biopesticide. In agricultural applications, biosurfactants can also be used as adjuvants to produce good wettability and even distribution of fertilizers and other applications on plant surfaces and in the soil.
- f) **Detergency and cleaning.** At the present time, essentially all surfactants used as commercial detergents and most other cleaning products are synthetic and can have toxic effects on freshwater organisms. Biosurfactants, as already pointed out, tend to be eco-friendly. They also exhibit good emulsifier properties with vegetable and mineral oils and good wetting of dirt and other particulates and therefore seem to have all of the qualities of a good detergent. Moreover, many biosurfactants are stable over a wide pH range (7.0–12.0) and show no loss of surfactant properties when they are heated to high temperatures. Their excellent compatibility and stability, therefore, favor their use in the formulation of laundry detergents. The largest barrier to that being the question of cost.
- g) **Food processing industry.** Although biosurfactants have not made headway as food additives or emulsifiers in the food industry, their well-proven surfactant properties mean that with time that may change. Besides the cost factor, a significant barrier to their use may be the question of approval by the various regulatory agencies around the world. For the time being, the “natural” surfactant banner will have to be carried by the almost natural surfactants such as the fatty acid esters containing glycerol, lecithin and its derivatives, sorbitan or ethylene glycol, and ethoxylated derivatives of monoglycerides discussed in more detail in Chapter 13. These surfactants are vital for improving the taste and overall organoleptic quality of food products, as well as extending the shelf life of those products with a minimum of health risks. Potential applications for biosurfactants in foods and food processing may lie well into the future for reasons unrelated to their potential as surfactants.
- h) **Cosmetics.** Biosurfactant are already carving out a niche in the health care and cosmetic industry due to their generally nonaggressive action with respect to human skin and other membranes. They are used as foaming agents, emulsifiers, solubilizers, wetting agents, cleansers, antimicrobial agents, mediators of enzyme action, etc. They can be found in insect repellents, acne pads, antacids, bath products, antidandruff products, contact lens solutions, baby products, mascara, lipsticks, and toothpastes, to name a few examples. Research into their potential uses continues.
- i) **Other.** Other potential applications of biosurfactants includes the pulp and paper industry, fabric dyeing, paints and surface protection, metal processing, and just about anywhere surfactants are employed.

4.5 Potential Limitations on the Commercial Use of Biosurfactants

Because of the complexity and potentially high production costs, the commercial use of biosurfactants on a large scale may be limited for some time. At the present time several biosurfactants such as rhamnolipids and surfactin are commercially available, but their availability and use are somewhat limited. Even in instances where the materials are available, even in limited quantities, their use may be restricted by the lack of regulatory approval. Rhamnolipids are the only biosurfactant family that has been approved by the US Environmental Protection Agency for use in agricultural and horticultural applications and by the FDA for use in pharmaceuticals, cosmetics, and food products.

4.6 Some Opportunities for Future Research and Development

Compared with normal synthetic surfactants, biosurfactants present many industrially attractive properties and advantages. However, they have not been extensively commercialized due to their relatively high production costs and lack of regulatory approval in most cases. The major operating costs in their production are fermentation and recovery. To overcome this, the use of concentrated carbon sources such as oleic acid can be an option for increased productivity during fermentation. The use of concentrated or “pure” carbon sources can be extremely expensive, however. A possible option for lowering fermentation cost, however, would be the use of “cheap” carbon sources such as process waste by-products. Different substances such as vegetable oils, animal fat, distillery and dairy wastes, sugar processing wastes, starch processing wastes, etc. can also be used as raw materials. Rhamnolipid production from olive oil mill wastes has been found to give excellent results. Biosurfactant production technology has improved significantly in recent years giving 10–20% yield improvements in productivity. However, more improvement is needed to get closer to economic competitiveness with synthetic surfactants.

Since downstream processing such as isolation, purification, and concentration costs are important, advancements in new, non-sterile technology will be needed. If such processes can be made economically feasible, it would be likely to cut overall costs significantly. Even more attractive would be if the downstream process could all be carried out in a single process step, the potential savings in time, product handling, transportation, etc., would be much more cost effective. That also means that the entire start-to-finish process would be more economically and ecologically attractive. Finally, most biosurfactant production is carried out on a laboratory or pilot plant scale using essentially sterile fermentation conditions. If technology could be developed to make the entire process a “one pot” operation, it would represent a real boon to the broad commercial insertion of biosurfactants into the surfactant market.

4.7 Some Observations About the Future of Biosurfactants

In spite of a great deal of success in biosurfactant production and identification on a small development scale, production at industrial scales remains a big challenge to the industry. The commercial production of any product depends on factors such as the availability of raw materials, production cost, and market demand. While current information indicates the market demand will almost

certainly exist, low productivity due to a lack of optimum raw materials and producer organisms, expensive downstream processing, and a lack of a good understanding of the details of bioreactor systems are important hurdles to be overcome in the industrial-level production of biosurfactants. The use of genetic engineering may make possible the development of “super” strains of producer organisms that would help lift the production of interesting biosurfactants to industrial levels. Of course, there will almost certainly be objections to moving in that direction from some groups, but due care should always be exercised. The development of new, more efficient processing technology, optimum fermentation substrates, etc. would probably also provide higher yields, as will the discovery of new biosurfactant options and a better understanding of the chemistry of biosurfactants. All of those goals, if and when they are reached, should place biosurfactants in a good competitive position to battle for market share in the world of surfactants.

5

Fluid Surfaces and Interfaces

From the viewpoint of the chemist or chemical technologist, a surface or an interface may be described as the boundary between at least two immiscible phases. In any such system, the boundaries between the phases may be of primary importance in determining the characteristics and behavior of the system as a whole, although the various bulk characteristics, in theory, are unaffected. The viability of many, if not most, scientific and commercial applications of multiphase systems depends on an ability to control and manipulate phase boundaries or interfacial interactions.

Geometrically, it is obvious that only a single surface can exist between two immiscible phases. If three phases are present, only a single line can be common among the various elements (Figure 5.1). Such geometrical considerations simplify the concepts needed to aid in understanding the fundamentals of surface activity. Once the physical and chemical concepts of a surface or interface are clear, it becomes easier to understand the role of surfactants in their modification. In what may be referred to as the “real” world, five basic types of interface are encountered: (i) solid–vapor (S/V), (ii) solid–liquid (S/L), (iii) solid–solid (S/S), (iv) liquid–vapor (L/V), and (v) liquid–liquid (L/L). Traditionally, interfaces involving one vapor and one condensed phase (e.g. S/V and L/V interfaces) are referred to as “surfaces.” In the following discussions that tradition will generally be followed, although “interfaces” may occasionally be used where generality is implied. Most obvious effects of surface-active agents on the physical properties of a system, to the untrained naked eye, are seen in systems where at least one phase is a liquid. The true importance of interfaces goes much deeper, however. As will hopefully become apparent in the following sections and chapters, the modification of an interface with less than a one molecule-thick layer may bring about dramatic changes in the nature of mixed phase systems.

Although adhesion and lubrication, with at least one solid phase, involve significant interfacial interactions and often employ the actions of surfactants, they also involve other physical phenomena that may ultimately be of greater importance to the system. They also quite often involve non-equilibrium conditions that make them difficult or impossible to analyze. The major portion of the subsequent discussions, therefore, will be concerned with conditions and systems in which the surface activity of the surfactant is of primary importance and usually under conditions at or near equilibrium. It must be recognized, however, that the modification of solid surfaces to control such characteristics as friction, water repellency, and static charging is becoming increasingly important and constitutes a broad area for potential surfactant application.

When one undertakes a discussion of surface and interfacial phenomena, several key points must be kept in focus. First, the requirements of mathematics and a touch of “common sense” cause most of us to visualize an interface as a sharp boundary or plane having a thickness of at

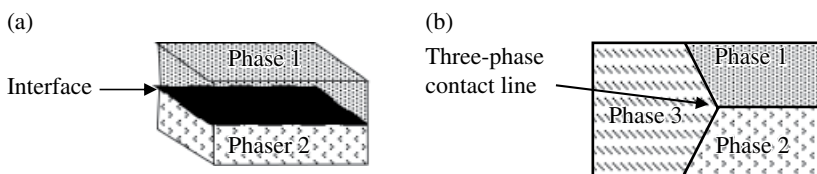


Figure 5.1 Geometrical considerations for the definition of interfaces: (a) the interface between two phases will be a plane or curved section; (b) the mutual interface among three phases will be a line, the three-phase contact line.

least one molecular diameter; the effect of the boundary in its simplest manifestation does not extend a great distance into either bulk phase. In more rigorous theoretical treatments, the interface may be assumed to be several molecules thick, **8**, and in some instances, the energetic consequences of the interface may extend several hundred nanometers into one or both phases.

Second, matter at an interface is usually found to have physical properties distinct from those of the bulk material, and as a result, a definite free energy is associated with each unit of interfacial area. In particular, atoms and molecules located at an interface will experience significantly different force fields from those in the bulk material because of different numbers and types of neighboring atoms and molecules.

A third characteristic of phase boundaries, especially those involving water, is the probable existence of an electrical potential across the interface. Although such charging phenomena are not always present, where they do exist they can be extremely important in determining the interfacial characteristics of the system. Electrostatic effects are most important in aqueous suspensions, dispersions, emulsions, foams, and aerosols in which one phase is very finely divided, creating a large interfacial area. The presence of electrical charges at interfaces often contributes significantly to the overall stability of a system. In addition, interfacial charges make possible many important industrial processes such as electrostatic paint and rubber deposition.

The interfacial energy and electrical characteristics of a system are determined by the usual quantities such as temperature and pressure and the chemical composition of the different phases. Charge characteristics may be altered significantly by the addition of ionic materials such as neutral electrolytes, by changes in the system pH, or by changes in the chemical composition of the aqueous phase, such as the addition of a water-miscible organic solvent that results in a change in the dielectric constant.

Interfacial energies will also be affected by other changes in phase compositions. Because of the relatively large distance between molecules, the nature of a contacting gas will normally have little effect upon the surface tension of a contacting liquid phase; however, if specific chemical or physical interactions are possible, some effect may be seen, especially for high-energy surfaces such as metals and metal oxides. The solubility of the gas in the liquid phase may also produce a change in the surface tension.

The surface tension or surface energy of a material, especially a liquid or high-energy solid, may be very significantly altered by small changes in its bulk composition. At interfaces between two condensed phases (e.g. liquid–liquid or liquid–solid), compositional changes in either or both phases may greatly alter the interfacial energy. Generally, the addition of a solute will change the surface tension of a liquid if the nature of the solute is such that its presence at the surface will result in a lower net free energy for the system (positive adsorption). Such an effect is especially important in liquids that have a relatively high surface tension, such as water. The presence of solutes may either raise or lower the surface tension at the liquid–vapor interface, although the

latter is normally observed. Interestingly, the presence of very small amounts of a surface-active organic molecule may lower the interfacial tension of water by 50% or more, while a fully saturated electrolyte solution may exhibit an increased surface tension of only a few millinewtons per meter (mN/m).

The liquid phase of most academic and industrial interest is water, which has a surface tension of between 72 and 73 mN/m at 20 °C. A 1% aqueous sodium hydroxide solution will have a slightly higher value of about 73 mN/m, while one of 10% will approach 78 mN/m. Relatively high concentrations of NaOH, or other electrolyte, are required to significantly increase the surface tension of water. The more normal result of dissolution of a material is to lower the surface tension of the liquid. In addition, the lowering effect is usually apparent at much lower concentrations than those required to raise the surface tension.

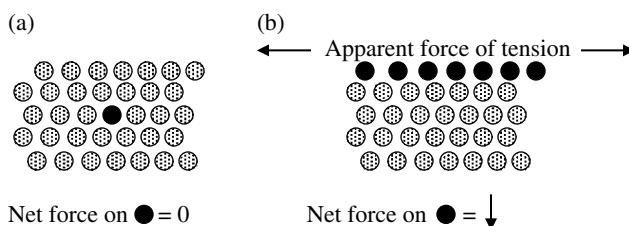
Conditions producing changes in surface tension at a liquid–vapor interface will usually also result in modification of the interfacial energy between the liquid and another liquid or a solid phase. In general, there will not be an obvious direct relationship between changes in the surface tension of a liquid phase and its other interfacial interactions under a given set of conditions. Nevertheless, the change in the surface tension of a liquid upon addition of a solute can be a qualitative indicator of changes to be expected in its interactions with other phases. The following chapters discuss in more detail the chemical and physical principles responsible for observed changes in interfacial interactions with the addition of solutes to one or more phases of a system.

5.1 Molecules at Interfaces

Atoms or molecules at an interface will have a higher potential energy than those in the bulk of a material as a result of their “geography.” Their location at the interface means that they will experience a net asymmetric force field due to interactions with neighboring units significantly different from units in the bulk (Figure 5.2). For two immiscible phases, surface or interfacial units will normally interact more strongly with identical units in the bulk rather than the “foreign” components in the adjacent phase. Because of the increased energy of units at the interface, thermodynamics demands that work is required to move them from the bulk phase to the surface. The minimum energy rule for systems in equilibrium will therefore lead to surface conditions yielding minimum interfacial area, or minimum asymmetric interactions.

Surface-active materials are those that, because of their characteristic molecular structures, are natural fence-sitters. Their split personalities drive them to reduce unfavorable energetic interactions by moving to more comfortable interfacial neighborhoods (adsorption), by getting together with their “own kind” (self-assembly or aggregation), or by simply getting out of town (precipitation or phase separation). When present in relatively low concentrations, they will preferentially adsorb at available interfaces, replace the higher-energy bulk phase molecules, and result in a net reduction in the free energy of the system as a whole.

Figure 5.2 Atoms (molecules) at interfaces – the origin of interfacial energy (a) bulk atoms or molecules and (b) surface atoms or molecules.



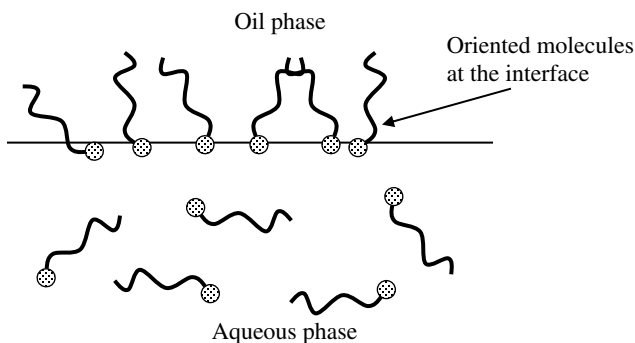


Figure 5.3 The preferential orientation of surfactant molecules at interfaces.

Surface-active materials possess a characteristic chemical structure that consists of (i) molecular components that will have little attraction for the solvent or bulk material, normally called the lyophobic group, and (ii) chemical units that will have a strong attraction for the solvent or bulk phase, called the lyophilic group (Figure 5.3). Although, in principle, surface activity and related concepts are applicable to any system composed of at least one condensed phase, the bulk of the scientific and technological literature is concerned with aqueous solvents and their interaction with a second phase. As a result, the term “hydrophobic” will quite often be employed in place of the more general “lyophobic”; analogously, “hydrophilic” will be employed instead of “lyophilic.” It should always be kept in mind, however, that generality is implied in most discussions, even when the specific terms applicable to water-based systems are used.

Materials that possess chemical groups leading to surface activity are generally referred to as being “amphipathic” or “amphiphilic.” When a material exhibiting the characteristics of surface activity is dissolved in a solvent (whether water or an organic liquid), the presence of the lyophobic group causes a distortion of the solvent liquid structure (and in principle that of a solid phase as well), increasing the overall free energy of the system. In an aqueous surfactant solution, for example, such a distortion of the water structure by the hydrophobic group increases the overall energy of the system and means that less work is required to transport a surfactant molecule to a surface or interface. The surfactant may therefore concentrate or preferentially adsorb at those locations, or it may undergo some other process to lower the energy of the system (e.g. aggregation or micellization). Since less work is required to bring surfactant molecules to the available interfaces, the presence of the surfactant decreases the work required to increase the interfacial area. The work per unit area required to form that new interface is the surface free energy or surface tension of the system, σ , usually reported in units of millinewtons per meter (mN/m) or dynes per centimeter in non-SI units. For solid surfaces, to be discussed in Chapter 12, the convention is to use millijoules per square meter (mJ/m²) or ergs per square centimeter (ergs/cm²).

The presence of a lyophilic group on the surfactant molecule prevents or retards the complete expulsion of the solute molecules from the solvent as a separate phase, at least at low concentrations. As discussed later in Chapter 7, higher concentrations of surfactant can lead to a number of interesting and useful phenomena.

The amphipathic structure of surfactant molecules not only causes the concentration of surfactant molecules at a liquid surface and consequent alteration of the surface energy but also causes the orientation of the adsorbed molecules to be such that the lyophobic groups are directed away from the bulk solvent phase. The resulting controlled molecular orientation produces some of the most important macroscopic effects observed for surface-active materials, as will be discussed in subsequent chapters. A discussion of the thermodynamics of surfactant adsorption phenomena

is presented in Chapter 7. For now, it is more important that the reader understands the qualitative relationships between the nature of interfaces and the general chemical structures required for a molecule to exhibit significant surface activity.

5.2 Interfaces and Adsorption Phenomena

The region of space lying at the boundary between two immiscible phases is generally referred to as the “interface” and represents a transition region in which the chemical and physical characteristics of one bulk phase undergo an abrupt (on a macroscopic scale) change to those of the adjacent one. On a microscopic scale, however, that change must occur over the distance of at least one, but more often several, molecular distances. To quantitatively treat the phenomena related to surface activity, especially adsorption phenomena, it is necessary to mathematically define the location of the dividing line or surface at which the change is assumed to occur.

For convenience, it is usually assumed that there exists a dividing surface defined as an ideal plane that lies between the two phases. Such a model is unrealistic, however, especially where adsorption at the interface occurs. Such an adsorbed film not only will possess a finite thickness related to the size of the adsorbed molecules but also will alter to some extent the thermodynamic environment of atoms or molecules of the two phases located in close proximity to the adsorbed species.

At this point it may be useful to reiterate that the general term “interface” refers to the above-mentioned boundary between any two phases: solid–solid (s/s), solid–liquid (s/l), solid–vapor (s/v), liquid–liquid (l/l), or liquid–vapor (l/v). In common usage, however, the term “surface” is used with reference to systems in which one phase is a gas, such as in the “surface tension” of a liquid. Throughout the subsequent discussions, the use of “interfacial” will imply applicability to multiple types of boundary region, while “surface” will apply only to the s/v and l/v systems.

5.2.1 A Thermodynamic Picture of Adsorption

In the consideration of adsorption processes, two aspects must be addressed: (i) the effect of the adsorbed species on the final equilibrium interfacial energy of the system and (ii) the kinetics of the adsorption process. For the most part, the discussions to follow are concerned only with equilibrium conditions, and dynamic processes are not addressed. For many surfactant applications, such a restriction will not result in significant limitations to the validity of the concepts involved. Obvious exceptions would be processes involving dynamic interfaces (i.e. coating operations).

If the idealized concept of a mathematical dividing plane between phases is employed to represent the interface, the adsorption of a solution component at the interface can conveniently be pictured as the existence at the interface of a concentration of the adsorbed material, n_i^s , that differs from its concentration, n_i^b , in one or both of the bulk phases, where *s* denotes the surface phase and *b* the bulk. The amount of component *i* in the surface phase in excess of that which would have been present had each phase extended up to the dividing plane S–S without changing composition is referred to as the “surface excess concentration” of *i*, Γ_i . Formally, it is given by

$$\Gamma_i = n_i^s/A \quad (5.1)$$

where *A* is the interfacial area. In principle, Γ_i may be either positive or negative, and its value will be determined by the somewhat arbitrary choice of the location of the dividing surface S–S.

When interfacial adsorption occurs, the energy of the interface changes. To understand and predict the role of surfactant adsorption, it is necessary to know the amount of material adsorbed at the interface of interest. The Gibbs equation, which relates changes in the interfacial energy of a system to the degree of adsorption of a species at the interface and the compositions of the bulk phases, forms the basis for understanding the thermodynamics of the adsorption process. Under conditions of constant temperature and pressure, the basic equation is given as

$$\delta\sigma_i = -\Gamma_1\delta\mu_1 - \Gamma_2\delta\mu_2 - \Gamma_3\delta\mu_3 - \dots \quad (5.2)$$

where σ_i is the interfacial energy, Γ_i is the surface excess of component i at the interface, and μ_i is its chemical potential in each bulk phase.

The change in the free energy G of a system may be given by

$$dG = -SdT + VdP + \delta dA + \sum \mu_i d\mathbf{n}_i \quad (5.3)$$

where G , S , P , V , and T have their usual thermodynamic meanings and A and \mathbf{n}_i are as defined above. At equilibrium and under constant conditions of T , P , and \mathbf{n}_i , Eq. (5.3) reduces to

$$dG = \sigma dA \quad (5.4)$$

If the surface excess of component i is allowed to vary by adsorption, then

$$\delta\sigma = -\sum (\mathbf{n}_i^s/A) d\mu_i = -\sum \Gamma_i \delta\mu_i \quad (5.5)$$

As pointed out above, the value of Γ_i is defined by the choice of the location of the dividing surface. To simplify the mathematics, it is convenient to define S-S so that the surface excess of one component, usually one of the bulk solvent phases, will be zero. For a simple two-component system (2 dissolved in 1, for example), Eq. (5.5) reduces to

$$\delta\sigma = -\sum \Gamma_2 \delta\mu_2 \quad (5.6)$$

The chemical potential of a species is related to its activity by

$$\mu_2 = \mu_2^0 + RT \ln a_2 \quad (5.7)$$

so that

$$d\mu_2 = RT d \ln a_2 \quad (5.8)$$

and

$$d\sigma = -\Gamma_2 RT d \ln a_2 \quad (5.9)$$

For dilute solutions where the activity coefficient of the solute is approximately 1, concentration c_2 can be substituted for a_2 . The Gibbs equation is then written in its most commonly encountered form

$$\Gamma_2 = -1/RT \left(d\sigma / d \ln c_2 \right) \quad (5.10)$$

In systems where the interfacial energy can be directly determined (in liquid-liquid and liquid-vapor systems, for example), Eq. (5.10) can be used to determine the surface excess concentration

of the adsorbed species and, in principle, to relate that quantity to the structure of the molecule. It therefore becomes a useful tool for characterizing a surfactant species at the molecular level and aids in the interpretation of surface phenomena on the basis of chemical composition and molecular structure. In systems where the interfacial energy cannot be measured directly – e.g. systems involving a solid interface – but the surface concentration can, the equation allows one to calculate changes in the interfacial energy of the system that would otherwise be inaccessible.

The form of Eq. (5.10) is general and can be encountered in several alternative formulations depending on the systems and interfaces in question. It is particularly important to remember that in the case of adsorbed species that are ionized, the adsorption of both ionic species (surfactant and counterion) must be taken into consideration. For a more complete derivation and explanation of the consequences of such a situation, the reader is referred to one of the references listed in the Bibliography for this chapter.

Liquid interfaces are normally well defined and, in principle, easier to handle on a theoretical basis than solid surfaces. As a result, interfaces involving liquid–liquid and liquid–gas phases have attracted a large portion of the attention devoted to the theoretical understanding of surfaces and interfaces. Such interfaces also constitute a large fraction of the practical applications of surfactants. Even taking into consideration their relative simplicity, liquid systems can involve a wide variety of interfacial phenomena. From a practical standpoint, the most important interfacial aspects of l/l and l/v systems are related to interfacial tension and the effects of adsorbed surfactants on that property. To have a concept of the role of surfactants at such interfaces, it is necessary to understand, in a qualitative way at least, the molecular forces involved.

5.2.2 Surface and Interfacial Tensions

The interfacial tension between a pure liquid and its vapor or between two immiscible or partially miscible liquids reflects the difference in the forces of attraction acting on molecules at the interface as a result of differences in the density or chemical compositions of the two phases. It has long been accepted that the existence of condensed phases of matter, especially the liquid state, is a result of van der Waals attractions between molecules. That is especially true for materials that do not possess any chemical structure that could lead to the action of forces of an electrostatic, dipolar, or other related specific character. For the sake of simplicity, consider a liquid whose molecules interact only through van der Waals or dispersion forces. In the bulk of the phase under consideration, all molecules will be surrounded by an essentially uniform force field, so that the net force acting on each will be zero. Molecules located at or near an interface, on the other hand, will experience a distorted field resulting in a net attraction for the surface molecules by the bulk. The unbalanced force of attraction acting on the surface molecules will cause the liquid to contract spontaneously to form, in the absence of gravity, a spherical drop.

To visualize the concept of the surface tension of a liquid, it is convenient to define it as a force acting tangentially to the surface at all points, the net result of which is the apparent formation of a surface “skin,” which contracts to confine the liquid into a shape of minimum interfacial area. Such a definition, while facilitating the understanding of the results of the phenomenon, may be misleading in the sense that no actual tangential force is acting at the surface of a pure liquid – it only produces the appearance of such a force. A more thermodynamically appropriate definition of surface tension and surface free energy is the work required to increase the area of a surface reversibly and isothermally by a unit amount. The interface between two immiscible liquids can be viewed similarly, except that the presence of a second, denser liquid phase will result in a less severe imbalance in the forces acting on the molecules at the interface and consequently a lower value for the interfacial tension.

Most commonly encountered room temperature liquids have surface tensions against air or their vapors that lie in the range of 10–80 mN/m. Liquid metals and other inorganic materials in the molten state will exhibit significantly higher values as a result of the much greater and more diverse interactions occurring in such systems. Water, the most important liquid we will consider, lies at the upper scale of what are considered to be normal surface tensions with a value in the range of 72–73 mN/m at room temperature, while hydrocarbons reside at the lower end, falling in the lower to middle 20's. The interfacial tension between water and a hydrocarbon liquid will fall somewhere between the surface tensions of the two phases. For reference purposes, some typical surface and interfacial tensions of liquids are listed in Table 5.1.

Modern treatments of van der Waals and related forces have made it possible to calculate with good accuracy the expected interfacial tensions of many systems that do not involve specific interactions such as dipoles and hydrogen bonding. While no further coverage of the more theoretical aspects of interfacial interactions is given here, a deeper understanding of the principles involved can aid greatly in the extension of the concepts covered to new systems and applications.

The concept of interfacial tensions given above is simplistic in the sense that it implies that the surface or interface is a static entity. In reality, there is a constant and, for liquids and gases, rapid interchange of molecules between the bulk and interfacial regions and between the liquid and vapor phases. If it is assumed that molecules leave the interfacial region at the same rate that they arrive, it is possible to estimate the exchange rate, b , of an individual molecule from the relationship

$$\beta = \alpha (2\pi m k T)^{1/2} p_0 \quad (5.11)$$

where α is the so-called sticking coefficient, p_0 is the equilibrium vapor pressure of the liquid, m the mass of the molecule, and k Boltzmann's constant. Assuming α to lie in the range of 0.03–1.0, a water molecule at 25 °C will have an average residence time of 3 μ s or less at the air–water interface. The corresponding residence time for a mercury atom would be roughly 5 ms, while that for a tungsten atom would be 10^{37} seconds at room temperature.

With such molecular mobility, it is clear that the surface of a pure liquid offers little resistance to forces that may act to change its shape. That is, there will be very little viscous or elastic resistance to the deformation of the surface. An obvious physical consequence of that fact is that a pure liquid will not support a foam for more than a small fraction of a second (see Chapter 11). A similar situation exists for the l/l interface. That fact, as we shall see in Chapter 6, has significant implications for many technological applications such as emulsions and foams, and it forms the basis for many of the most important applications of surfactants.

Table 5.1 Typical surface and interfacial tensions of liquids at 20 °C.

Liquid	Surface tension (mN/m)	Interfacial tension (vs water, mN/m)
Water	72.8	
<i>n</i> -Octane	21.8	50.8
Benzene	28.9	35.0
<i>n</i> -Octanol	27.5	8.5
Mercury	485	375

Because of the mobility of molecules at fluid interfaces, it is not surprising to find that temperature can have a large effect on the interfacial tension of a system. As the temperature of a system is increased, the surface tension of almost all liquids will decrease. From Eq. (5.3), it is clear that a negative temperature coefficient for the surface free energy indicates that the surface excess entropy is positive. At temperatures near the critical temperature of the liquid, the cohesive forces acting between molecules in the liquid become very small, and the surface tension approaches zero. While it is intuitively attractive to assume that molecules at a surface possess more degrees of freedom and are more disordered and, possibly, that the surface region has a lower density than the bulk liquid, finding the proper choice for a model has made the calculation of surface configurational entropy difficult. A number of empirical equations that attempt to predict the temperature coefficient of surface tension have been proposed, with one of the most useful being that of Ramay and Shields:

$$\sigma(\mathbf{M}\mathbf{x}/\rho)^{2/3} = \mathbf{k}_s(\mathbf{T}_c - \mathbf{T} - 6) \quad (5.12)$$

where \mathbf{M} is the molar mass of the liquid, ρ its density, \mathbf{T}_c the critical temperature, and \mathbf{k}_s a constant applicable for almost all materials (a commonly used value is $2.1 \times 10^{-7} \text{ J/K/mol}^{2/3}$). There do exist a few exceptions to the observation of negative temperature coefficients, but such exceptions are found in molten metal and metal oxide melts, where the atomic and molecular interactions are much more complex.

5.2.3 The Effect of Surface Curvature

Because so many applications of surfactants involve surfaces and interfaces with high degrees of curvature, it is often important to understand the effect of curvature on interfacial properties. What is usually considered to be the most accurate procedure for the determination of the surface tension of liquids, the capillary rise method, depends upon a knowledge of the relationship between surface curvature and the pressure drop across curved interfaces. Because of the existence of surface tension effects, there will develop a pressure differential across any curved surface, with the pressure being greater on the concave side of the interface. That is, the pressure inside a bubble will always be greater than that in the continuous phase. The Young–Laplace equation:

$$\Delta p = \sigma(1/r_1 + 1/r_2) \quad (5.13)$$

in which Δp is the drop in pressure across a curved interface, \mathbf{r}_1 and \mathbf{r}_2 are the principal radii of curvature, and σ is the surface or interfacial tension, relates the quantities of interest in this situation. For a spherical surface where $\mathbf{r}_1 = \mathbf{r}_2$, the equation reduces to

$$\Delta p = 2\sigma/r \quad (5.14)$$

For a very small drop of liquid in which there is a large surface-to-volume ratio, the vapor pressure will be higher than that over a flat surface of equal area. The movement of liquid from a flat interface into a volume with a curved interface will require the input of energy into the system, since the surface free energy of the curved volume will increase. If the radius of a drop is increased by $d\mathbf{r}$, the surface area will increase from $4\pi\mathbf{r}^2$ to $4\pi(\mathbf{r} + d\mathbf{r})^2$, or by a factor of $8\pi\mathbf{r}d\mathbf{r}$. The free energy increase will be $\sigma \times 8\pi\mathbf{r}d\mathbf{r}$. If during the process δn moles of liquid are transferred from the flat phase with a vapor pressure of \mathbf{p}_o to the drop with vapor pressure \mathbf{p}_r , the free energy increase will also be given by

$$\Delta G = \delta nRT \ln(\mathbf{p}_r/\mathbf{p}_o) \quad (5.15)$$

Equating the two relationships leads to what is known as the *Kelvin equation*:

$$RT \ln(p_r/p_o) = 2M\sigma/\rho r = 2V_m\sigma/r \quad (5.16)$$

In Eq. (5.16), ρ is the density, M the molar mass, and V_m the molar volume of the liquid. It can be shown that extremely small radii of curvature can lead to the development of significant pressure differences in drops. For a drop of water with a radius of 1 nm, the partial pressure ratio from Eq. (5.15) will be about 3. It is obvious, then, that the condensation of molecules in systems where the seed nuclei are exceedingly small will be retarded by a relatively high-energy barrier. Such a relationship helps greatly in explaining the ability of many liquid and vapor systems to become supersaturated. It is the input of energy by scratching, agitation, etc., or the provision of a seed site of sufficient size, that brings about the rapid condensation or crystallization of the system.

5.2.4 The Surface Tension of Solutions

In the most general sense, the “surface tension” of a liquid refers to the equilibrium excess surface energy at the boundary between the liquid and its own vapor. In practice, the vapor phase will usually be a mixture of the vapor and other gases such as air. The difference, however, is not significant for most purposes. When the liquid phase is not a pure liquid, but a homogeneous mixture (solution) of two or more components, it seems intuitively obvious that the surface tension of the system should be some mathematical average of that of the two pure components. The simplest such combination for a binary mixture would be an additive combination related to the quantity of each component in the mixture, such as mole fraction. The relationship may be written as

$$\sigma_{\text{mix}} = \sigma_1 X + \sigma_2 (1 - X) \quad (5.17)$$

where σ_{mix} is the surface tension of the solution, σ_1 and σ_2 are the surface tensions of the respective components, and X is the mole fraction of component 1 in the mixture. In ideal systems where the vapor pressure of the solution is a linear function of the composition, such relationships are found. Normally, however, there will be some positive or negative deviation from linearity, with the latter being most commonly encountered. Some examples of the variation of the surface tension of mixtures with composition are shown in Figure 5.4.

Taking water as an example, when the second component of a mixture is a solute such as an inorganic electrolyte or other material that requires significant solvation, relationships between surface tension and composition can be expected to be quite varied, depending on the exact nature of the solute–solvent interaction. It is generally found, for example, that the addition of inorganic electrolyte to water results in an increase in the surface tension of the solution, although the effect is not dramatic and requires rather high salt concentrations to become significant (Figure 5.5). The relative effectiveness of cations at increasing the surface tension of water generally follows the Hofmeister series: $\text{Li}^+ > \text{Na}^+ > \text{K}^+$, and $\text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$.

Unlike the inorganic electrolytes, the presence of an organic material in aqueous solution will result in a decrease in the surface tension of the system. The extent of such lowering will depend upon a number of factors including the relative miscibility of the system (or the solubility of the organic solute) and the tendency of the organic material to preferentially adsorb at the water–air interface. Liquids such as ethanol or acetic acid result in slight, gradual decreases in the surface tension of their aqueous solutions, while longer-chain organics such as 1-butanol can produce more dramatic effects (Figure 5.6). When the organic solute has a limited solubility in water, the effect on surface tension becomes characteristic of surfactant solutions, where a minimum

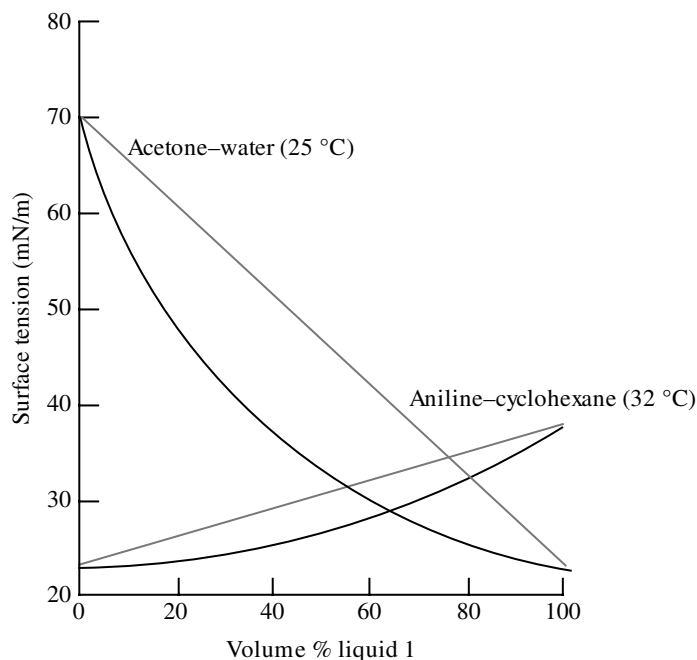


Figure 5.4 The variation of surface tension of various liquid mixtures.

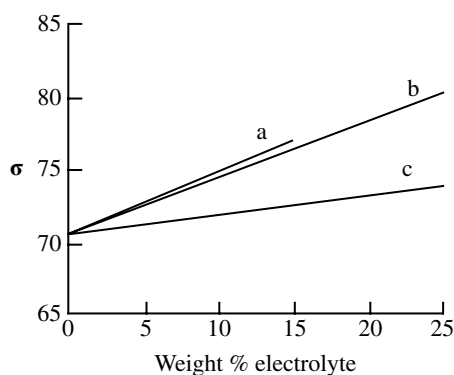


Figure 5.5 The effects of simple electrolytes on the surface tension of water: (a) LiCl, (b) NaCl, and (c) NaBr.

value of σ will be obtained as the solute concentration increases before surface saturation or some form of solute behavior change (precipitation, micelle formation, etc.) prevents further change in the surface tension.

5.2.5 Surfactants and the Reduction of Surface Tension

As previously stated, the measurement of the surface tension of a surfactant solution is possibly one of the most common physical properties of such solutions used to characterize the properties of surfactants in general. Since the surface tension of a liquid is determined by the energy of the molecules in the interfacial region, the displacement of surface liquid molecules by adsorbed solute will directly affect the measured value. It is the relationship between the chemical structure of

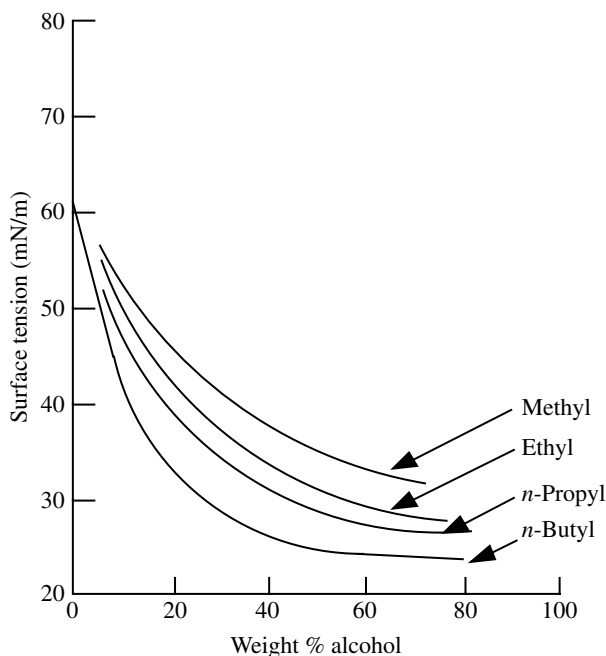


Figure 5.6 The effect of added alcohols on the surface tension of aqueous solutions.

an adsorbing molecule and the rate and extent of adsorption under given circumstances that differentiates the various surfactant types and determines their utility in applications where surface tension lowering is of importance.

In aqueous solutions, the interface between liquid and vapor phases involves interactions between relatively densely packed, highly polar water molecules and relatively sparse, nonpolar gases. The result is an imbalance of forces acting on the surface molecules and the observed high surface tension of water (72.8 mN/m). If the vapor phase is replaced by a condensed phase such as octane, which has a higher molecular density but still interacts only by nonpolar (i.e. dispersion) forces, the interfacial energy as given by the interfacial tension will be reduced significantly (52 mN/m). If the extent of molecular interaction between phases can be increased by the introduction of polar groups, as, for instance, in 1-octanol, the interfacial energy reduction will be even greater (8.5 mN/m). Clearly, then, any alteration in the nature of the molecules composing the liquid surface would be expected to result in a lowering of the interfacial energy between the adjacent phases. Therein lies the explanation for the action of surfactants in lowering the surface and interfacial tension of aqueous solutions. It also explains why most surfactants will not affect the surface tension of organic liquids – the molecular natures of the liquid and the surfactant are not sufficiently different to make adsorption particularly favorable, or if adsorption occurs, the energy gain is not sufficient to produce a measurable change in surface tension. The actions of fluorocarbon- and siloxane-based materials are exceptions.

The molecular characteristics necessary for a material to perform as a surfactant in aqueous solution have already been extensively discussed. It is useful, however, to reiterate the basic functions of the molecular groups to promote an understanding of their effects on the liquid surface tension. The hydrophilic group, of course, serves the purpose of imparting sufficient water solubility to the molecule to provide a workable concentration of surfactant to produce the desired result. Monolayers of insoluble organic compounds will lower the surface tension of water, but such monolayers must be applied as a separate phase and are not practical for most applications. A significant exception might be the application of materials to prevent or retard evaporation of water from reservoirs.

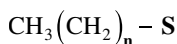
In such cases, however, the desired result does not rely on the reduction of surface tension, but on the formation of a barrier to retard the passage of water molecules from the liquid to the vapor phase. The hydrophobic group of a surfactant must play two essential roles: (i) to provide the proper solubility properties, so that the molecules will be preferentially adsorbed at the water/vapor interface, and (ii) to alter the energy of interaction between the liquid interface and the contacting gas molecules. Each function will be directly related to the chemical nature of the hydrophobic group and, in some cases, to that of the hydrophile. The specifics of the relationships between chemical structure and activity at the water–vapor interface are discussed in more detail below.

When hydrocarbon-based surfactants are dissolved in polar organic media such as the lower alcohols, in which they have an appreciable solubility, the reduction in surface tension will be small or nonexistent, since the nature of the interface is not changed significantly by the adsorption of surfactant molecules. Most nonpolar organic liquids are similarly unaffected by the presence of the more common surfactants, since the surfactants usually have very limited solubility in such solvents and the pure organic liquid will usually have a lower interfacial energy than that which would be produced by the adsorption of surfactant molecules. The exceptions to this rule, as noted above, are the siloxane and fluorinated surfactants, which do, in some cases, produce significant surface tension lowering effects in organic media.

5.2.6 Efficiency, Effectiveness, and Surfactant Structure

In a discussion of the performance of a surfactant in lowering the surface tension of a solution, it is necessary to consider two aspects of the process: (i) the concentration of surfactant required to produce a given surface tension reduction and (ii) the maximum reduction in surface tension that can be obtained, regardless of the concentration of surfactant present. The two effects may be differentiated by defining the surfactant “efficiency” as that bulk phase concentration necessary to reduce the surface tension by a predetermined amount, commonly 20 mN/m, and its “effectiveness” as the maximum reduction that can be obtained by the addition of any quantity of surfactant.

The extent of reduction of the surface tension of a solution depends on the substitution of surfactant for solvent molecules at the interface. Therefore, the relative concentration of surfactant in the bulk and interfacial phases should serve as an indicator of the adsorption efficiency of a given surfactant and as a quantitative measure of the activity of the material at the solution–vapor interface. For a given homologous series of straight-chain surfactants in water



where **S** is the hydrophilic group and **n** is the number of methylene groups in the chain, an analysis based on the thermodynamics of transfer of a surfactant molecule from the bulk phase to the interface that leads to the conclusion that the so-called efficiency of adsorption will be directly related to the length of the hydrophobic chain. If the energy of such transfer can be divided into components related to that for the terminal methyl group in a straight-chain molecule ($\Delta G_{\text{trm}} - \text{CH}_3$), subsequent methylene groups ($\Delta G_{\text{trm}} - \text{CH}_2 -$), and the hydrophilic group ($\Delta G_{\text{trs}} - \text{S}$) and a standard reduction level of 20 mN/m is chosen, the surfactant efficiency can be defined as the negative logarithm of the bulk phase concentration required to produce a reduction of 20 mN/m, so that

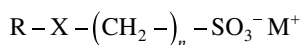
$$-\log(\text{C})_{20} = \text{pC}_{20} = \text{n}(-\Delta G_{\text{trm}}/2.3\text{RT}) + (-\Delta G_{\text{trs}}/2.3\text{RT}) + \text{K} \quad (5.18)$$

where **K** = $-\Delta G_{\text{trm}}$. For a given head group **S** under constant conditions of temperature, solvent composition, etc., the equation reduces to a direct dependence of efficiency on the length of the hydrocarbon chain **n**.

Since the surfactant efficiency is directly related to the thermodynamics of chain transfer from bulk to interface, it is reasonable to expect that chain modifications that alter that characteristic; that is, changes in the hydrophobic character of the surfactant would produce parallel changes in the value of pC_{20} . The linear relationship between the number of methylene linkages in a chain and the adsorption efficiency for a variety of hydrophilic groups is illustrated in Figure 5.7.

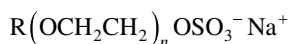
Branching in the hydrophobic group will result in a reduction in the hydrophobicity of a surfactant chain relative to that of a related straight-chain material with the same total carbon content. It is found, for example, that carbon atoms located on branch sites will contribute approximately two thirds as much to the character of a surfactant molecule as one located in the main chain. Similar results are observed for surfactants with two or more shorter chain hydrophobes of equal total carbon content (e.g. internal substitution of the hydrophilic group) and for the presence of unsaturation in the chain. The phenyl group will usually contribute an effect equivalent to approximately 3.5 methylene groups.

If a surfactant possesses two polar groups, as do, for example, the taurines or sulfoesters



where R is a normal surfactant hydrophobe and X is an amide or ester linkage, the methylene groups lying between the two polar groups that will contribute an effect equivalent to approximately half that found for such groups located in R.

Although usually thought of as hydrophilic, the first oxyethylene group attached to the hydrophobic chain in surfactants of the type



where $n < 4$ actually appears to behave in a manner suggestive of the addition of approximately 2.5 methylene groups to the hydrophobic chain. Such anomalous behavior might be attributed to changes in the solvation of the ether linkage brought on by the close proximity of the highly solvated sulfate group. Succeeding OE groups appear to have little or no significant effect on the hydrophobicity of the molecule. Sulfated polyoxyethylene surfactants having $n > 4$, as do most of the commercially important members of this class, are usually composed of several POE chain

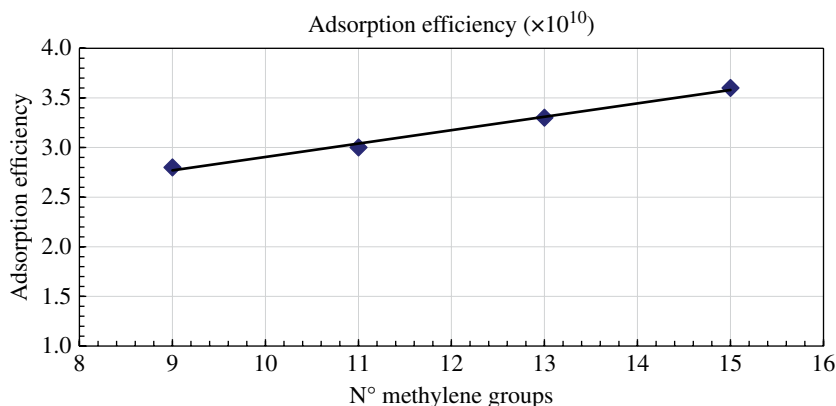


Figure 5.7 The effect of hydrocarbon chain length (as $-CH_2-$ groups) on the adsorption efficiency of sodium sulfonate surfactants.

lengths and do not lend themselves to an analysis of the effects of the POE units. If single isomer materials were available, it is quite likely that an interesting combination of effects would be found.

In nitrogen-based cationic surfactants, it has generally been found that the presence of short-chain alkyl groups (fewer than four carbon atoms) attached to the nitrogen seem to have little effect on the efficiency of adsorption of the molecule. The dominant factor will always be the length of the primary hydrophobic chain. That effect is true whether the alkyl groups are attached to a quaternary ammonium group, an amine oxide, or a heterocyclic nucleus such as pyridine.

The nature of the charge on an ionic surfactant has a small effect on the efficiency of surfactant adsorption. It is primarily the hydrophobic group that predominates. Some effect will, however, be seen if the counterion to the primary charge is one that is highly ion paired: that is, one that is not highly solvated in the system and therefore produces a lower net electrical charge as the molecules are adsorbed at the interface. The addition of neutral electrolyte to a surfactant solution will produce a similar result in increasing the efficiency of adsorption of a given surfactant.

When one considers the efficiency of adsorption of nonionic surfactants, it must be remembered that significant differences in the electrical nature of the hydrophilic group can be expected to result in considerable change in the manner in which they adsorb at a solution–vapor interface. For POE surfactants with the same hydrophobic group and an average of 7–30 OE units, the efficiency of adsorption at the solution–vapor interface has been found to adhere to an approximately linear relationship of the form

$$pC_{20} = A_{tr} + nB \quad (5.19)$$

where A_{tr} and B_{tr} are constants related to the free energy of transfer of $-\text{CH}_2-$ and OE groups, respectively, from the bulk phase to the interface, and n is the number of OE units in the POE chain. As is usually the case for POE nonionics, most data reported have been obtained using non-homogeneous POE chains. The available data indicate that the efficiency of adsorption will decrease slightly as the number of OE units on the surfactant increases.

Up to this point, we have seen that the efficiency of surfactant adsorption at the solution–vapor interface, the bulk concentration required to produce a given level of surface tension lowering, is dominated by the nature of the hydrophobic group and is relatively little affected by the hydrophilic head group. It is often found that the second characteristic of the adsorption process, the so-called adsorption effectiveness, will be much more sensitive to other factors and will quite often not parallel the trends found for adsorption efficiency.

The choice of 20 mN/m as a standard value of surface tension lowering for the definition of adsorption efficiency is convenient but somewhat arbitrary. When one discusses the effectiveness of adsorption, as defined as the maximum lowering of surface tension regardless of surfactant concentration, the value of σ_{min} is determined only by the system itself and represents a more firmly fixed point of reference. The value of σ_{min} for a given surfactant will be determined by one of two factors: (i) the solubility limit or Krafft temperature (T_K) of the compound or (ii) the **cmc**. In either case, operationally the maximum amount of surfactant adsorbed will be reached at the maximum bulk concentration of free surfactant, assuming one can ignore the slight decreases in g found for some surfactants above the **cmc**.

Because the activity of surfactants used below T_K cannot reach the theoretical maximum as determined by the thermodynamics of surfactant aggregation, the surfactants will also be unable to achieve their maximum degree of adsorption at the solution–vapor interface. It is therefore important to know the value of T_K for a given system before considering its application. Most surfactants, however, are employed well above their Krafft temperature, so that the controlling factor for the determination of their effectiveness will be the **cmc**.

When one examines the shape of the σ - $\ln C$ curve for a surfactant, it can be seen that the curve becomes approximately linear at some concentration below the **cmc**. It can be shown that the effectiveness of the adsorption of a surfactant, $\Delta\sigma_{\text{cmc}}$, can be quantitatively related to the concentration of surfactant at which the Gibbs equation becomes linear, C_1 , the surface tension attained at C_1 , namely, σ_1 , and the **cmc**. The relationship has the general form

$$-\Delta\sigma_{\text{cmc}} = (\sigma_o - \sigma_1) + 2.3\Omega RT\Gamma_m \log(C_{\text{cmc}}/C_1) \quad (5.20)$$

where σ_1 is the surface tension of the pure solvent and Γ_m is the maximum in surface excess of adsorbed surfactant at the interface. The factor Ω in Eq. (5.20) is related to the number of molecular or atomic units that will be adsorbed at the interface with the adsorption of each surfactant molecule. For nonionic surfactants or ionic materials in the presence of a large excess of neutral electrolyte, $\Omega = 1$; for ionic surfactants $\Omega = 2$, since one counterion must be adsorbed for each surfactant molecule, giving a total of two species.

Equation (5.20) shows that the effectiveness of a surfactant at lowering the surface tension of a solution is related to three main factors: (i) the **cmc** of the surfactant; (ii) the surfactant concentration required to attain the surface tension at which Gibbs equation linearity begins, C_1 ; and (iii) the maximum surface excess concentration of the surfactant, Γ_m , at surface saturation. The effectiveness of a surfactant can be conveniently quantified by using a value of C_1 at which the surface tension has been reduced by 20 mN/m, assuming $\Gamma_{20} \approx \Gamma_m$ so that the two concepts of efficiency and effectiveness can be directly linked quantitatively.

Application of Eq. (5.20) then allows for the calculation of a standard quantity, **cmc**/ C_{20} , which serves as a useful measure of overall surfactant effectiveness. Some representative values that illustrate the effects of well-controlled changes in surfactant structure are given in Table 5.2.

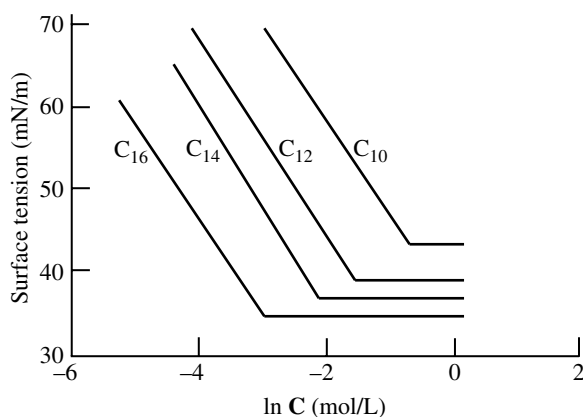
It is often found that the efficiency and effectiveness of surfactants at lowering the surface tension of a solution do not run parallel; in fact, it is commonly observed that materials that produce significant lowering of the surface tension at low concentrations are more efficient, will be less effective, and will have a smaller Γ_m . This follows from the complex relationship between adsorption at the interface and micelle formation in the solution.

On a molecular basis, the conflicting factors can be seen conceptually as arising from the different roles of the molecular structure in the adsorption process. Surfactant efficiency is related to the extent of adsorption at the interface as a function of bulk surfactant concentration. At a concentration well below the **cmc**, efficiency can be structurally related to the hydrophobicity of the surfactant tail and the nature of the head group. For a given homologous series of surfactants, it will be a function of the thermodynamics of transfer of the hydrophobic tail from the bulk to the surface phase. A plot of σ vs. $\ln C$ for such a series will exhibit a relatively regular shift in the linear portion of the curve to lower concentration as methylene groups are added to the chain. An idealized example of such a series is shown in Figure 5.8.

While the role of molecular structure in determining surfactant efficiency is primarily thermodynamic, its effectiveness is more directly related to the size of the hydrophobic and hydrophilic portions of the adsorbing molecules. When one considers the adsorption of molecules at an interface, it can be seen that the maximum number of molecules that can be fitted into a given area will depend upon the area occupied by each molecule. That area will, to a good approximation at least, be determined by either the cross-sectional area of the hydrophobic chain or the area required for the arrangement for closest packing of the head groups (Figure 5.9), whichever is greater. For straight-chain 1 : 1 ionic surfactants, it is usually found that the head group requirement will predominate, so that for a given homologous series, the surface tension minimum obtained will vary only slightly with the length of the hydrocarbon chain.

Table 5.2 Experimental values of cmc/C_{20} , Γ_{20} , and σ_{\min} for some typical surfactants in aqueous solution.

Surfactant	Temperature ($^{\circ}\text{C}$)	cmc/C_{20}	$\Gamma_{20} (\times 10^{10} \text{ mol}/\text{cm}^2)$	$\sigma_{\min} (\text{mN}/\text{m})$
$\text{C}_{12}\text{H}_{25}\text{SO}_4^- \text{Na}^+$	25	2.0	3.3	40.3
$\text{C}_{12}\text{H}_{25}\text{SO}_3^- \text{Na}^+$	25	2.3	2.9	40.8
$\text{C}_{12}\text{H}_{25}\text{SO}_4^- \text{Na}^+$	60	1.7	2.6	44.8
$\text{C}_{12}\text{H}_{25}\text{SO}_3^- \text{Na}^+$	60	1.9	2.5	43.9
$\text{C}^{16}\text{H}_{33}\text{SO}_4^- \text{Na}^+$	60	2.5	3.3	37.8
$\text{C}_{12}\text{H}_{25}\text{C}_6\text{H}_4\text{SO}_3^- \text{Na}^+$	70	1.3	3.7	47.0
$p\text{-C}_{12}\text{H}_{25}\text{C}_6\text{H}_4\text{SO}_3^- \text{Na}^+$	75	1.6	2.8	48.8
$\text{C}_{16}\text{H}_{33}\text{C}_6\text{H}_4\text{SO}_3^- \text{Na}^+$	70	1.9	1.9	45.0
$\text{C}_{12}\text{H}_{25}\text{C}_5\text{H}_5\text{N}^+\text{Br}^-$	30	2.1	2.8	42.8
$\text{C}_{14}\text{H}_{29}\text{C}_5\text{H}_5\text{N}^+\text{Br}^-$	30	2.2	2.8	41.8
$\text{C}_{12}\text{H}_{25}\text{N}(\text{CH}_3)_3^+\text{Br}^-$	30	2.1	2.7	41.8
$\text{C}_{10}\text{H}_{21}(\text{POE})_6\text{OH}$	25	17.0	3.0	30.8
$\text{C}_{12}\text{H}_{25}(\text{POE})_6\text{OH}$	25	9.6	3.7	31.8
$\text{C}_{16}\text{H}_{33}(\text{POE})_6\text{OH}$	25	6.3	4.4	32.8
$\text{C}_{12}\text{H}_{25}(\text{POE})_9\text{OH}$	23	17.0	2.3	36.8
$\text{C}_{16}\text{H}_{33}(\text{POE})_9\text{OH}$	25	7.8	3.1	36.8
$\text{C}_{12}\text{H}_{25}(\text{POE})_{12}\text{OH}$	23	11.8	1.9	40.8
$\text{C}_{16}\text{H}_{33}(\text{POE})_{12}\text{OH}$	25	8.5	2.3	39.8
$\text{C}_{16}\text{H}_{33}(\text{POE})_{15}\text{OH}$	25	8.9	2.1	40.8
$\text{C}_{16}\text{H}_{33}(\text{POE})_{12}\text{OH}$	25	8.0	1.4	45.8
$p\text{-}t\text{-C}_8\text{H}_{17}\text{C}_6\text{H}_4(\text{POE})_7\text{OH}$	25	22.9	2.9	30.8

Figure 5.8 A schematic representation of the effects of hydrophobe chain length on surfactant cmc and σ_{\min} .

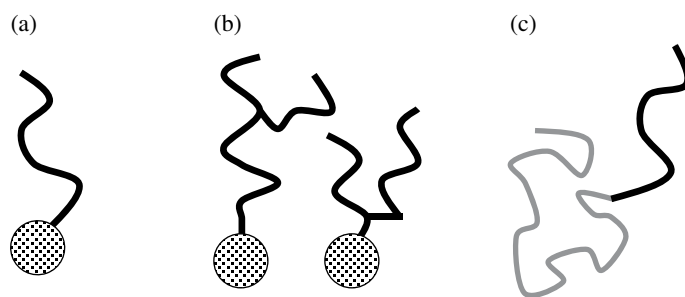


Figure 5.9 Schematic representation of the role of the hydrophobe in determining the effectiveness of surfactant adsorption: (a) *n*-alkyl, area determined by head group; (b) branched or double-tailed, area determined by bulk of tail relative to head; (c) polyoxyethylene nonionic, area determined by coiling of POE chain.

Since the decrease in surface tension obtained is directly related to the surface excess adsorption of the surfactant by the Gibbs equation, a reduction in the amount of material that can be adsorbed in a given surface area will reduce the ultimate surface tension lowering attained. The efficiency will change more or less regularly with the chain length. The sign of the charge on the ionic surfactant has only a minor effect on the ultimate surface tension attained, indicating that the geometric requirements (including electrostatic effects) are relatively constant from one head group to the next. In the presence of neutral electrolyte, of course, electrostatic repulsions between adjacent molecules will be reduced, making their effective areas smaller. The net result will be a slight increase in surfactant effectiveness.

The complex relationship between the molecular structure of a surfactant and its impact on surfactant efficiency and effectiveness can be illustrated by the case of a series of nonionic POE surfactants in which the number of OE units is held constant and the hydrocarbon chain length is increased (Table 5.3). In the series it is found that the surface excess at surface saturation Γ_m

Table 5.3 The effect of polyoxyethylene and hydrocarbon chain length on the efficiency and effectiveness of surface tension lowering for a number of POE nonionic surfactants with the general formula $R(POE)_nOH$.

R	<i>n</i>	$\Gamma_m (\times 10^{10} \text{ mol/cm}^2)$	$\sigma_{\text{min}} (\text{mN/M})$
C ₆	6	2.7	32.8
C ₁₀	6	3.0	30.8
C ₁₂	6	3.7	31.8
C ₁₆	6	4.4	32.8
	7	3.8	33.8
	9	3.1	36.8
	12	2.3	39.8
	15	2.1	40.8
	21	1.4	45.8
<i>p,t</i> -C ₈ H ₁₇ C ₆ H ₄	7	2.9	30.8
	8	2.6	32.8
	9	2.5	34.3
	10	2.2	35.8

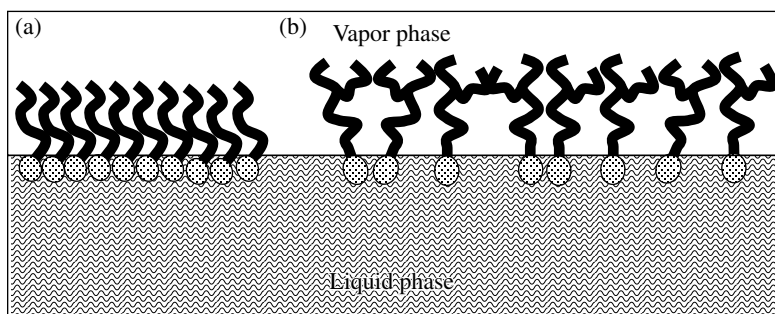


Figure 5.10 The role of surfactant structure and packing in the determination of packing efficiency and surface tension: (a) straight-chain hydrophobes, closest packing and maximum effectiveness, area per molecule determined by head group, and (b) branched, unsymmetrical, substituted, etc., tails reduce packing efficiency, area determined by tail.

decreases regularly from 4.4×10^{-10} mol/cm² for C₁₆ to 2.7×10^{-10} for C₆, while the σ_{\min} remains relatively constant. This would indicate that while the efficiency of surfactant adsorption is increasing with the length of the hydrocarbon chain, the overall effectiveness of the material is relatively unchanged.

It can be seen from Table 5.3 that in the cases of the C₁₆ and *p,t*-C₈H₁₇-C₆H₄ hydrophobic groups, as the size of the hydrophilic group (*n*) increases, the effectiveness (as σ_{\min}) decreases. This effect can be related to the fact that each additional OE group added to the head of the surfactant increases the total area required for adsorption of the molecule, reduces the packing density of hydrophobic groups at the interface, and therefore results in a smaller reduction in the surface tension of the system. If the area per molecule a_o required for the adsorption of the C₁₆H₃₃(POE)_{*x*} series of surfactants is examined (Table 5.3), it can be seen that the addition of each OE unit increases the requirement by an average of 0.5 nm². From insoluble monolayer experiments, it has been shown that the surface tension (or surface pressure $\pi = \sigma_o - \sigma$) is related to the orientation of the adsorbed molecules at the interface, with maximum lowering resulting from an essentially perpendicular orientation between hydrophobe and interface. For soluble monolayers such as those in question here, that orientation will be directly affected by the proximity of the neighboring molecules (Figure 5.10a); thus, factors that cause an increase in molecular separation will also allow the adsorbed molecules to tilt more relative to the surface, producing a smaller effective surface tension reduction (Figure 5.10b).

While an increase in the hydrocarbon chain length in a series of normal alkyl surfactants between C₈ and C₂₀ will have a minor effect on the effectiveness of a surfactant, other structural changes can produce much more dramatic effects. We have seen that structural features such as branching and multiple-chain hydrophobes will generally result in increases in the **cmc** of surfactants with the same total carbon content. Those changes seem to have a much smaller effect on the efficiency of the surfactant (C₂₀) than on its effectiveness. For sodium *n*-dodecylbenzene sulfonate the **cmc** and σ_{\min} were 1.2×10^{-3} M and 36 mN/m, while the same values for sodium (2-methyl undecylbenzene) sulfonate were 2.3×10^{-3} M and 27 mN/m, respectively.

The introduction of slightly polar groups such as unsaturation, ether, ester, or amide linkages or hydroxyl groups located well away from the head group will usually result in a significant lowering of both the efficiency and effectiveness of the surfactant as compared with a similar material with no polar units. Such a result has generally been attributed to changes in orientation of the adsorbed molecule with respect to the surface due to interactions between the polar group and the water

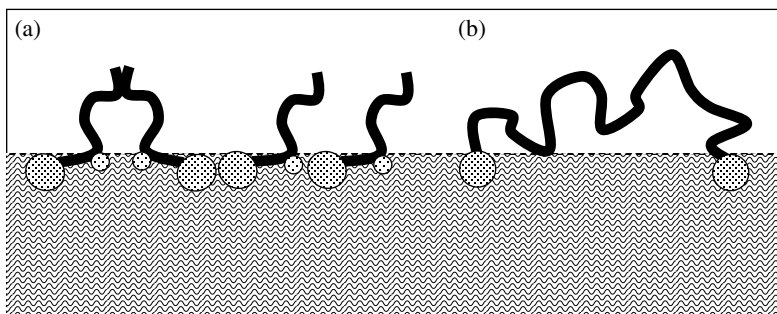


Figure 5.11 The effect of additional polar groups on the adsorption of surfactants: (a) additional polar groups along the hydrophobic chain and (b) multiple, separated head groups.

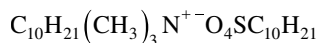
(Figure 5.11). If the polar group is situated very near to the primary hydrophilic group, its orientational effect will be much less dramatic, although it may still have a significant effect on the **cmc** of the material.

Changes in the hydrophobic group in which fluorine atoms are substituted for hydrogen will usually result in significant increases in the efficiency and effectiveness of the surfactant. The substitution of fluorine for hydrogen in a straight-chain surfactant results in a relatively small increase in chain cross-sectional area, as compared with a methyl branch, for example, so that the changes must be related to the chemical nature of the substitution. As has already been pointed out, fluorinated organic materials have a relatively low cohesive energy density and therefore little interaction with adjacent phases, or themselves, for that matter. They therefore have very favorable thermodynamic driving forces for adsorption (leading to high efficiency), as well as low surface energies. Their effectiveness is reflected in the very low surface tension values produced (as low as 20 mN/m in some instances).

Thus far, the discussion has dealt primarily with the effects of changes in the hydrophobic group on the ability of a surfactant to reduce the surface tension of a solution. It was stated earlier that an ionic head group usually plays a relatively minor role in determining the efficiency and effectiveness of a surfactant. While that may be true for groups closely related in size and electrostatic character, alterations in those factors can produce significant changes in their activity at the solution–air interface. A class of surfactants well suited to the study of such effects is that of the quaternary ammonium salts in which three of the alkyl groups are short-chain units such as methyl, ethyl, and propyl. The substitution of propyl for methyl groups in *n*-tetradecyltrimethylammonium bromide resulted in a significant reduction in the efficiency of adsorption while not affecting the minimum surface tension obtained. Presumably, the presence of the bulkier propyl substituents on the head group greatly increases its area per molecule and therefore reduces its adsorption efficiency.

In the case of anionic head groups, there appear to be only relatively minor variations in effect from one group to another. The difference in cross-sectional area between sulfate and sulfonate groups does not appear to influence greatly the activity of surfactants in lowering surface tensions, although some difference can be noted when differences in **cmc** are taken into consideration. The role of the counterion can be important when changes result in significant alterations in the ion binding properties of the molecule. Tight ion binding will reduce the extent of electrostatic repulsion between adsorbed molecules, allowing for tighter packing of surfactant at the interface and, in general, increases in both the efficiency and the effectiveness of the surfactant. A similar result is obtained by the addition of neutral electrolyte.

An interesting class of surfactants that has found practical application because of their tight ion binding and its effects on surface activity is those in which both the anion and the cation of the pair are, individually, surface active. Materials such as *n*-decyl trimethylammonium *n*-decylsulfate (written in reverse to illustrate the ion binding)



have been found to be much more efficient and effective at surface tension reduction than either simple material alone. The very strong ion pairing nature of their association results in a high packing density at the interface and large values for σ_{20} and σ_{\min} . Related materials were found to lower the surface tension of a solution to approximately 24 mN/m, one of the lowest surface tensions yet reported for totally hydrocarbon surfactant systems.

As has already been mentioned, the effect of changes in the hydrophobic chain length on the effectiveness of surface tension reduction in nonionic surfactants is relatively minimal. Increases in the length of the polyoxyethylene chain, on the other hand, lead to significant reductions in the effectiveness of a given surfactant hydrophobic group. It appears, then, that the primary factor involved in the efficiency and effectiveness of nonionics in these cases is the length of the hydrophilic chain. A similar result could be expected for other types of nonionic material, although there are few good experimental data available to warrant excessive generalization.

The discussion above introduced the basic concepts related to the interfacial energy of fluid–fluid interfaces, particular the liquid–vapor interface. The practical effects of surface tension lowering were not addressed because they generally appear in the context of phenomena such as emulsification, foaming, wetting, and detergency, to be discussed later. For further details on the subject of surface tension lowering and surfactant adsorption at fluid interfaces, the reader is referred to the works cited in the Bibliography.

6

Surfactants in Solution

Self-Assembly and Micelle Formation

The amphiphilic nature of surfactants causes them to exhibit many properties that appear on first sight to be somewhat contradictory. Because of their special molecular structures, they possess something of a “love–hate” relationship in most solvents, resulting in a tug of war among competing forces striving for a comfortable (energetically speaking) accommodation within a given environment. Surfactants, one might say, appear to feel to some extent that the grass is greener on the other side of the fence, and as a result, they spend much of their time sitting on that “fence” between phases. Some of the basic characteristics of those “fences” were introduced in Chapter 5. This chapter will begin the process of expanding on the specifics of how surfactant molecular structures affect their surface activity. At this point, it is important to understand some of the more important aspects of the solution behavior of surfactants and some of the circumstances that can affect that behavior.

In their energetic drive to minimize unfavorable interactions or to maximize favorable interactions with their environment, surfactants spend much of their time at interfaces or associating with others of their own kind. The purpose of the discussions here is to introduce some of the more important and useful fundamental concepts of surfactants in solution, as we currently understand them. A basic understanding of these concepts can help guide a prospective surfactant user in understanding a given phenomenon and choosing a material that may suit a particular need. This chapter will concern itself primarily with the more simple – if that term can be applied in the present context – aspects of surfactant activity in terms of self-assembled or spontaneous, thermodynamically driven aggregate structures in solution. As is usually the case with surfactant-related discussions, the primary emphasis will be placed on aqueous systems. Chapter 7 will give a broad introduction to the more complex and highly ordered self-assembled structures such as vesicle, bi- and multiplayer membranes, continuous bilayer systems, liquid crystals, etc. All of those areas are becoming more important in current and potential technological and research applications of surfactants and other amphiphiles.

Surfactants participate in processes of self-assembly that almost makes them seem “alive,” in that they form specific assembled structures that depend on their environment and can spontaneously transform into a different, but related structure as their “living conditions” change. The formation of the self-assembled structures, for example, does not result from the input of energy such as in commutation or emulsification; it is a spontaneous association process resulting from the energetics of interaction between the individual units and the solvent medium, as is crystallization. However, the size, shape, and basic nature of the associated structure are controlled by a complex series of factors distinctly different from those involved in crystallization. The size,

in particular, will be much more limited than that of a normal crystal. This class of colloids is generally referred to as association or self-assembled colloids.

This class of association colloids can be further divided into several subgroups, which include micelles, vesicles, microemulsions, and bilayer membranes. Each subgroup of association colloids plays an important role in many aspects of colloid and surface science, both as theoretical probes that help us to understand the basic principles of molecular interactions, and in many practical applications of those principles, including biological systems, medicine, detergency, crude oil recovery, foods, pharmaceuticals, and cosmetics. Before undertaking a discussion of the various types of association colloids, it is important to understand the energetic and structural factors that lead to their formation.

6.1 Surfactant Solubility

The specific structures of surfactant molecules, having well defined lyophilic and lyophobic components, are responsible for their tendency to adsorb at interfaces and in doing so reduce the interfacial free energy of the system in which they are found. Those structures will also be important in determining the solubility of the substance in the continuous phase – usually aqueous. If a material is not sufficiently soluble to reach a minimum concentration in the system, it will not be present in sufficient quantity to perform the interfacial tasks for which it is intended. A molecule with the same elemental composition, but a different structural distribution of its constituent atoms may show little or no surface activity.

The primary mechanism for energy reduction in most cases will be adsorption at the available interfaces. However, when all interfaces are, or begin to be, saturated, the overall energy reduction may continue through other mechanisms as illustrated in Figure 6.1. The physical manifestation of one such mechanism is the crystallization or precipitation of the surfactant from solution – that is, bulk phase separation such as that seen for a solution of any solute that has exceeded its solubility limit. In the case of surfactants, alternative options include the formation of molecular

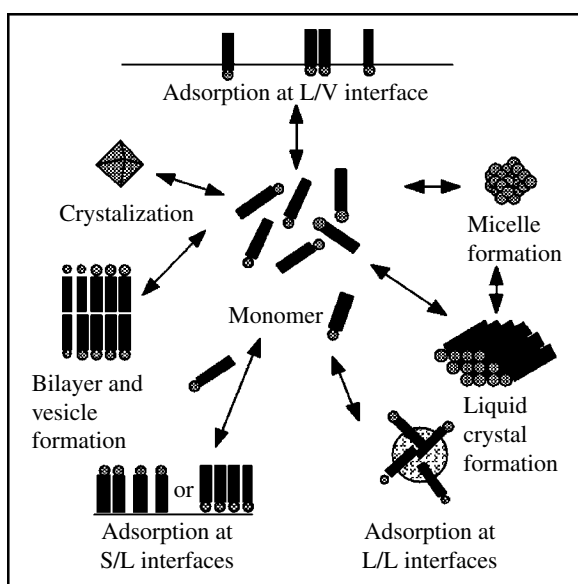


Figure 6.1 Modes of surfactant action for the reduction of surface and interfacial energies.

aggregates such as micelles and liquid crystal mesophases that remain in solution as thermodynamically stable, dispersed species with properties distinct from those of the monomeric solution. Before turning our attention to the subject of micelles, it is necessary to understand something of the relationship between the solubility of a surfactant or amphiphile in the solvent in question and its tendency to form micelles or other aggregate structures.

For most pure solutes, solubility is a more or less “yes or no” question. Under a given set of conditions of solvent and temperature, and sometimes pressure, the solute has a specific solubility limit that, when passed, results in the formation of crystals or at least a distinct separate phase that can hypothetically be separated from the solvent or supernatant liquid by physical means. While crystalline hydrates may be separated from water solutions, they will normally have specific compositions that make them unique and subject to characterization by chemical analysis, for example. Surfactants and other amphiphiles, on the other hand, can exhibit a number of intermediate or mesophases in going from a dilute solution of individual or “independent” molecules to crystalline hydrates or anhydrous structures. A hypothetical “spectrum” of surfactant mesophases in aqueous solution is given in Figure 6.2.

As pointed out in Chapter 1, a primary driving force for the industrial development of synthetic surfactants was the problem of the insolubility of the fatty acid soaps in the presence of multivalent cations such as calcium and magnesium or at low pH. While most common surfactants have a substantial solubility in water, that characteristic changes significantly with changes in the length of the hydrophobic tail, the nature of the head group, the electrical charge of the counterion, the system temperature, and the solution environment. For many ionic materials, for instance, it is found that the overall solubility of the material in water increases as the temperature increases. That effect is the result of the physical characteristics of the solid phase – that is, the crystal lattice energy and heat of hydration of the material being dissolved.

For ionic surfactants, it is often observed that the solubility of a material will undergo a sharp, discontinuous increase at some characteristic temperature, commonly referred to as the Krafft temperature, T_K . Below that temperature, the solubility of the surfactant is determined by the

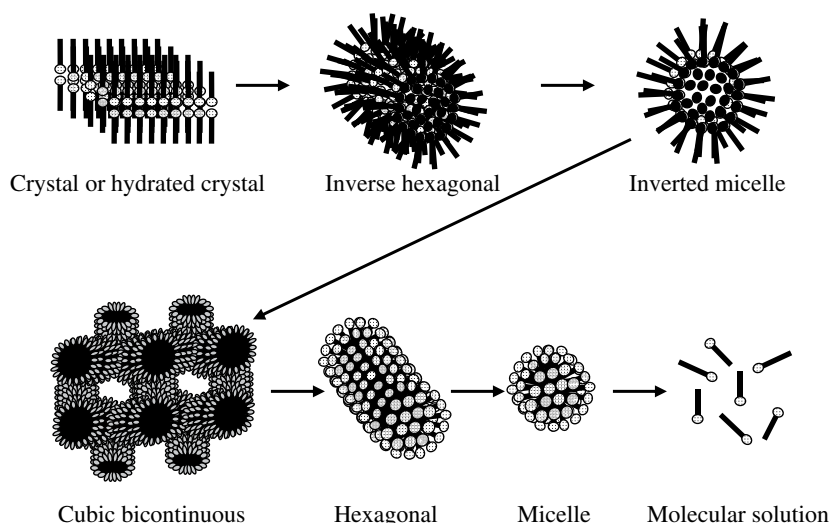


Figure 6.2 A hypothetical spectrum of surfactant mesophases in aqueous solution as formed with increased water content.

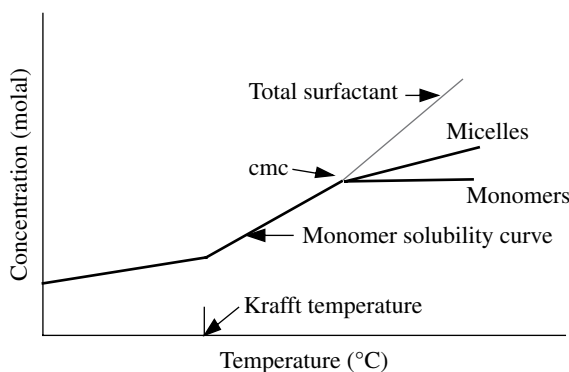


Figure 6.3 Temperature/solubility relationship for typical ionic surfactants.

crystal lattice energy and the heat of hydration of the system. The concentration of the monomeric species in solution will be limited to some equilibrium value determined by those properties. Above T_K , the solubility of the surfactant monomer increases to the point at which self-assembled aggregate formation may begin, and the aggregated species – a micelle, for example – becomes the thermodynamically favored or predominant form in solution.

The micelle may be viewed, to a first approximation, as structurally resembling the solid crystal or a crystalline hydrate, so the energy change in going from the crystal to the micelle will be less than the change in going to the monomeric species in solution. Thermodynamically, then, the formation of micelles favors an overall increase in solubility. The concentration of surfactant monomer may increase or decrease slightly at higher concentrations (at a fixed temperature), but micelles will be the predominant form of surfactant present above a critical surfactant concentration, the critical micelle concentration or **cmc**. The apparent solubility of the surfactant, then, will depend not only on the solubility of the monomeric material but also on the solubility of the micelles or other aggregate structures. A schematic representation of the temperature/solubility relationship for ionic surfactants is shown in Figure 6.3.

The Krafft temperatures of a number of common ionic surfactants are given in Table 6.1. It can be seen from the data that T_K can vary as a function of both the nature of the hydrophobic group and the character of the ionic interactions between the surfactant and its counterion. It should be noticed that no data are listed for nonionic surfactants. Nonionic surfactants, because of their different mechanism of solubilization, do not exhibit a Krafft temperature. They do, however, have a characteristic temperature/solubility relationship in water that causes them to become less soluble as the temperature increases. In some cases, phase separation occurs, producing a cloudy suspension of surfactant. The temperature (usually a range of temperature) at which the phases separate is referred to as the “cloud point” for that surfactant. More will be said about that later.

The intimate relationship between the Krafft temperature and the solid state of the surfactant is confirmed by the good correlation between T_K for a surfactant of a given chain length and the melting point of the corresponding hydrocarbon material. Such correlations can also be found for the appearance of other structural changes in surfactant solutions. As we shall see in later chapters, good practical use can be made of such temperature-related phenomena. Note that in Table 6.1 fluorinated surfactants have Krafft temperatures in roughly the same temperature range as hydrocarbon materials containing twice as many carbon atoms. That tendency is seen, not surprisingly, in comparing most surfactant properties of hydrocarbon against fluorocarbon materials.

As indicated above, an important characteristic of a surfactant in solution is its solubility relative to the critical concentration at which thermodynamic considerations result in the onset of

Table 6.1 The Krafft temperatures, T_k , of typical ionic surfactants.

Surfactant	T_k (°C)
$C_{12}H_{25}SO_3^- Na^+$	38
$C_{14}H_{29}SO_3^- Na^+$	48
$C_{16}H_{33}SO_3^- Na^+$	57
$C_{12}H_{25}OSO_3^- Na^+$	16
$C_{14}H_{29}OSO_3^- Na^+$	30
$C_{16}H_{33}OSO_3^- Na^+$	45
$C_{10}H_{21}CH(CH_3)C_6H_4SO_3^- Na^+$	32
$C_{12}H_{25}CH(CH_3)C_6H_4SO_3^- Na^+$	46
$C_{14}H_{29}CH(CH_3)C_6H_4SO_3^- Na^+$	54
$C_{16}H_{33}CH(CH_3)C_6H_4SO_3^- Na^+$	61
$C_{16}H_{33}OCH_2CH_2OSO_3^- Na^+$	36
$C_{16}H_{33}(OCH_2CH_2)_2OSO_3^- Na^+$	24
$C_{16}H_{33}(OCH_2CH_2)_3OSO_3^- Na^+$	19
$C_{10}H_{21}COOC(CH_2)_2SO_3^- Na^+$	8
$C_{12}H_{25}COOC(CH_2)_2SO_3^- Na^+$	24
$C_{14}H_{29}COOC(CH_2)_2SO_3^- Na^+$	36
$C_{10}H_{21}OOC(CH_2)_2SO_3^- Na^+$	12
$C_{12}H_{25}OOC(CH_2)_2SO_3^- Na^+$	26
$C_{14}H_{29}OOC(CH_2)_2SO_3^- Na^+$	39
$n-C_7F_{15}SO_3^- Na^+$	56
$n-C_8F_{17}SO_3^- Li^+$	<0
$n-C_8F_{17}SO_3^- Na^+$	75
$n-C_8F_{17}SO_3^- K^+$	80
$n-C_8F_{17}SO_3^- NH_4^+$	41
$n-C_7F_{15}COO^- Li^+$	<0
$n-C_7F_{15}COO^- Na^+$	8
$n-C_7F_{15}COO^- K^+$	26
$n-C_7F_{15}COO^- NH_4^+$	2

molecular aggregation or micelle formation. Since micelle formation is of critical importance to many surfactant applications, the understanding of the phenomenon relative to surfactant structures constitutes an important element in the overall understanding of surfactant structure–property relationships.

6.2 The Phase Spectrum of Surfactants in Solution

Most academic discussions of surfactants in solution concern themselves with relatively low concentrations, so the system contains what may be called “simple” surfactant species such as monomers and their basic aggregates or micelles. Before entering into a discussion of micelles, however,

it is important to know that although they have been the subject of exhaustive studies and theoretical considerations, they are only one of the several states in which surfactants can exist in solution. A complete understanding of surfactant solution systems, including correlations between chemical structures and surface properties, requires a knowledge of the complete spectrum of possible states of the surfactant. While no attempt is made here to provide a detailed discussion of surfactant phase behavior, it is important that the subject be at least introduced into any description of the solution behavior of surface-active agents.

When one considers the wide range of possible environments for surfactant molecules in the presence of solvents, it is not surprising that the subject can appear overwhelming to the casual observer. As illustrated in Figure 6.2, the possibilities range from the highly ordered crystalline phase to the dilute monomeric solution that, although not completely without structure, has order only at the level of molecular dimensions. Between the extremes lie a variety of phases whose natures depend intimately on the chemical structure of the surfactant, the total bulk phase composition, and the environment of the system (temperature, pH, co-solutes, etc.). Knowledge of those structures, and of the reasons for and consequences of their formation, influences both our academic understanding of surfactants and their technological application.

Many pure surfactants, especially ionic materials and specific types of nonionics, can be made to crystallize relatively easily, while others, because of their chemical makeups, will solidify into basically amorphous solids with no detectable crystal structure. Because of their amphiphilic nature, a surfactant crystal structure always appears to be lamellar, somewhat like a multilayer cake, with alternating head-to-head and tail-to-tail arrangements (Figure 6.4). The energy of the surfactant crystal, as reflected by its melting point, for example, will be primarily determined by the chemical structure of the molecules. Some types may have several possible crystal structures that arise depending on the conditions under which crystallization was carried out. In those cases, one of the structures will be more thermodynamically stable, and the other structures will over time convert to that stable form. It may take some time, but it will happen in the absence of some “outside” retarding factor. More will be said about that in later chapters.

Terminally substituted *n*-alkyl sulfates, for example, will have higher melting points than the corresponding branched or internally substituted materials basically due to the more compact and ordered packing structures available to the straight-chain materials. Additionally, highly polar, small hydrophilic groups will provide enhanced crystal stability over bulky, more polarizable functionalities.

The packing of long hydrocarbon chains into a crystalline alignment is difficult because of the many possible variations in configuration for the units of the chain due to rotation about the four

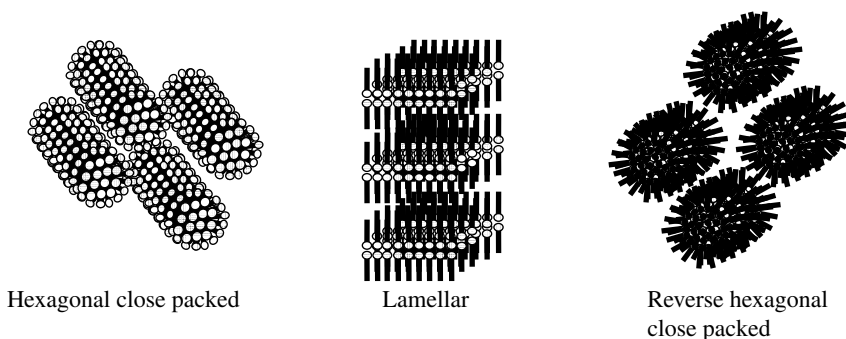


Figure 6.4 Typical arrangement of surfactant molecules in liquid crystalline structures.

bonds to each carbon atom (rotational isomers). That difficulty is reflected in the relatively low melting points and poorly defined crystal structure of most hydrocarbons under normal conditions. When members of a homologous series or structural isomers are present as a mixture, a situation common to many important surfactant systems, the difficulty of crystal formation is magnified. The crystallization of pure surfactants from a mixture, therefore, can be difficult, especially if the mixture is that of a series of homologues. For that reason, crystals of natural fatty acid soaps, commercial polyoxyethylene (POE) nonionic surfactants, and other surfactants containing homologous species or branched isomers are rare, and even relatively pure samples may exhibit a variety of crystal structures depending on the conditions of crystallization.

When surfactants are crystallized from water and other solvents that are strongly associated with the polar head group, it is common for the crystalline form to retain a small amount of solvent in the crystal phase. In the case of water, the material would be a hydrate. The presence of solvent molecules associated with the head group allows for the existence of several unique compositions and morphological structures that, although truly crystalline, are different from the structure of the anhydrous crystal.

As water or other solvent is added to a crystalline surfactant, the structure of the system will undergo a transition from the most highly ordered crystalline state to one of greater disorder usually referred to as a liquid crystalline or “mesophase.” In such phases some structure is retained in one molecular region of the system, while a more liquid or amorphous structure is developed in the other. Such crystalline/amorphous phases, of which 18–20 have been reported for some molecular structures, are characterized by having some physical properties of both crystalline and fluid phases. These phases will have at least one highly ordered dimension and, as a result, will exhibit relatively sharp X-ray diffraction (XRD) patterns and optical birefringence. In other dimensions, the phases will behave in a manner more similar to non-structured or minimally structured fluids.

Two general classes of liquid crystalline structures or mesophases are encountered whether one is considering surfactants or other types of material. These classes are the thermotropic liquid crystals, in which the structure and properties are determined by the temperature of the system, and lyotropic liquid crystals in which the structure is determined by specific interactions between the surfactant molecules and the solvent. With the exception of the natural fatty acid soaps, experimental data support the view that almost all surfactant liquid crystals are lyotropic in nature.

Theories on liquid crystal formation predict the existence of at least 18 distinct liquid crystalline structures for a given molecular composition and structure. Nature, however, appears to have been kind in that only three of those possibilities have been identified in simple, two-component surfactant–water systems. The same is often true for three-component surfactant–oil–water systems. The three liquid crystalline phases usually associated with surfactants are the lamellar, hexagonal, and cubic. Of the three, the cubic phase is the most difficult to define and detect. It has been invoked to describe the new kid on the block in surfactant aggregates, the so-called “cubosomes.” A little more will be said about them later. It may have a wide variety of structural variations that involve components of the other mesophases. The remaining two types are more easily characterized and, as a result, are better understood.

The lamellar liquid crystal can be viewed as a mobile or “plasticized” derivative of the basic surfactant crystalline phase. The hydrophobic chains in these structures possess a significant degree of freedom or randomness, unlike the case in the crystalline phase, in which the chains are usually locked into the all-trans configuration (for terminally substituted *n*-alkyl hydrophobes). The level of disorder of the lamellar phase may vary smoothly or change abruptly as solvent is added, depending on the specific system. It is therefore possible for a surfactant to pass through

several distinct lamellar phases. Because the basic unit is bilayer structure, lamellar phases are usually uniaxial. The lamellar phase resembles the bilayer and multilayer membranes to be discussed later, although they are formed as a result of changes in solvent concentration rather than the specific molecular structural features of the surfactant.

The hexagonal liquid crystal is a high viscosity fluid phase composed of a close-packed array of cylindrical assemblies of theoretically unlimited size in the axial direction. The structures may be “normal” (in water) in that the hydrophilic head groups are located on the outer surface of the cylinder, or “inverted,” with the hydrophile located internally.

As mentioned before, surfactant liquid crystalline phases are normally lyotropic. The characteristics of the system, then, are highly dependent on the nature and amount of solvent present. In a phase diagram of a specific surfactant, the liquid crystalline phases may span a broad range of compositions and may constitute by far the major fraction of all possible compositions. With the continued addition of water or other solvent, the system will eventually pass through the regions of the mesophases into the more familiar isotropic solution phase. The liquid state is the most highly random condition of condensed matter and, as a result, tends to have fewer easily detected structural features. Surfactant solutions, however, are far from devoid of structure; it is only the scale of the structure that changes as dilution occurs.

The addition of a third (or fourth) component such as a water-immiscible oil, electrolyte, or a polar non-surfactant solute to an aqueous surfactant solution can lead to the formation of new phases with distinct properties. These new components will alter the thermodynamic balance of the system and, as a result, may alter the nature of the aggregated species present. The extent of their effect will vary with concentration, structural features, and specific interactions; however, under the proper conditions they will give rise to important new structures and phases not encountered in a simple two-component system. The factors controlling the nature of the system will no longer be simply those of the solvent and solute but will involve complex three-way (or more) interactions.

The natures and properties of the multicomponent systems are discussed in somewhat more detail in the following chapters. They are introduced here only to complete the discussion of the “spectrum” of surfactant structures commonly encountered. One thermodynamically interesting phase consisting of surfactant, water, oil, and sometimes a fourth “co-surfactant” component is referred to as the “microemulsion” region of the multicomponent phase diagram. There is still some controversy as to the exact nature of microemulsions, since structures in this region seem to span the size range from conventional micelles (with diameters of a few nanometers) to the more easily defined emulsions (several hundred nanometers). Should microemulsions be considered a new, separate phase or simply an extension of the micellar phase in which the basic structure is enlarged by the presence of an additive incorporated into the micelle? There are reasonably compelling arguments that support the idea of microemulsions as a phase separate from the normal swollen micelle, particularly the question of size. Other factors make it less easy to separate the two systems into distinct classes. In the final analysis, trying to define a boundary between micelles and microemulsions is much like trying to define the wavelength at which light changes from red to orange. It will probably be a question of convenience or individual personal preference (or the pronouncement of some august international body).

Conventional emulsions, unlike the microemulsions, are easily identified as dispersions of one liquid phase in another. In such systems, the energetics of surfactant aggregation is not a major factor in their formation. Conventional emulsions, therefore, are only indirectly related to the subject of this chapter. They are, however, related in the sense that a direct line of evolution can be drawn from the crystalline surfactant phase, through the mesophases, micelles, and microemulsions, to emulsions, all resulting from changes in the composition of the system.

In addition to facilitating our understanding of the fundamental principles of surfactant solution behavior, knowledge of the details of the solution properties of a surfactant can be of great importance. From a practical standpoint, a great deal can be achieved by understanding solution phase diagrams of surfactants. Of particular importance is the understanding of structure–solubility relationships, the selection of optimum components for a given product application, the understanding of the details of surface and interfacial activity, and the design of new surfactant molecular structures for optimal performance in both old and new applications. The major drawbacks of such studies are that they require a significant amount of time and experimental effort and they are only really useful, in general, for pure, single-component, well-characterized surfactant systems – something not very common in most technological applications.

Although the study of surfactant solution properties throughout the complete concentration range is of obvious theoretical and occasional practical importance, no attempt is made to cover in detail those phases more structured than the simplest aggregates of surfactants in dilute solution. For more information on surfactant phase diagrams, the reader is referred to the works cited in the Bibliography.

6.3 The History and Development of Micellar Theory

The self-assembly or aggregation of surfactants into micelles in dilute solutions, as we will see, is a direct consequence of the thermodynamic requirements of the particular surfactant–solvent system under consideration. It has been suggested that phases occurring between the simplest micelles and true crystals are natural consequences of the removal of water from the micellar system, but do not constitute thermodynamically distinct states. That is, the factors determining the structures of the mesophases are identical to those that control the formation of micelles in the first place. The same would be true of aggregates other than micelles, which do not fall under the classification of mesophases.

The number of publications related to micelles, micelle structures, and the thermodynamics of micelle formation is enormous. Extensive interest in the phenomenon of the self-association of surface-active species is evident in such wide-ranging chemical and technological areas as organic and physical chemistry, biochemistry, polymer chemistry, pharmaceuticals, petroleum recovery, minerals processing, cosmetics, and food science. In addition to the general scientific literature, hundreds of patents have been issued covering new materials and uses related to micelle formation and the effects of those structures on different phenomena of potential commercial interest. Even with the vast amount of experimental and theoretical work devoted to the understanding of the aggregation of surface active molecules, no theory or model has emerged that can unambiguously satisfy all the evidence and all the interpretations of that evidence.

Early in the twentieth century, it was recognized that aqueous solutions of surface-active agents do not follow the patterns of solution behavior common to most solutes as their concentration is increased. It was suggested that the unusual behavior of surfactants could be attributed to the aggregation of individual molecules into clusters in solution above a fairly well-defined concentration. Although that somewhat radical idea received a rather cool initial reception, the concept of molecular aggregation in solution eventually began to develop a significant following, and today everyone accepts it as fact. Micelles have now been studied with almost every technique devised by modern science including XRD, nuclear magnetic resonance (NMR), electron spin resonance (ESR), small-angle neutron scattering (SANS), light scattering, fluorescence, calorimetry, and many other solution and spectroscopic techniques. Despite being probed, prodded, and picked

apart, however, micelles have still refused to yield the ultimate data, the interpretation of which is universally accepted and which unequivocally defines the true nature and characteristics of the aggregated species. It is possible, of course, that the diversity of surfactant structures and micellar and related aggregate species (vesicles, bilayers, microemulsions, etc.) are such that only very general laws will be found to be applicable to all; perhaps each system will have its specific twists, which preclude the existence of a “universal theory of everything” for surfactant aggregation, although in the generally ordered scheme of natural phenomena, such a prospect is unlikely. However, in science as in many human endeavors, it is as much the thrill of the hunt as the final capture that supplies the driving force for our activities.

It is generally accepted that most surface-active molecules in aqueous solution can aggregate into structures or clusters averaging 30–200 monomeric units in such a way that the hydrophobic portions of the molecules are closely associated and mutually protected from extensive contact with the bulk of the water phase. Not so universally accepted are some of the ideas concerning micellar shapes, the nature of the interior of a micelle, the “roughness” of the aggregate surface, the sites of adsorption of additional solutes into (or onto) micelles, and the size distribution of micelles in a given system. Although sophisticated experimental techniques continue to provide new insights into the nature of micelles, we still have things to learn. Given the inherent tendency of scientists to question and refine experimental procedures and to offer alternative interpretations for the results, it seems likely that questions concerning the theory of micelle formation and a complete model of the molecular nature of micelles will remain “fair game” for some time to come.

6.3.1 Manifestations of Micelle Formations

Early in the study of the solution properties of surface active materials, it became obvious that the bulk solution properties of such materials were unusual and could change dramatically over very small concentration ranges. The measurement of properties such as surface tension, electrical conductivity, or light scattering as a function of surfactant concentration produces property curves that normally exhibit relatively sharp discontinuities at comparatively low concentration (Figure 6.5). The sudden change in a measured property is interpreted as indicating a significant change in the nature of the solute species affecting the measured quantity. In the case of the measurement of

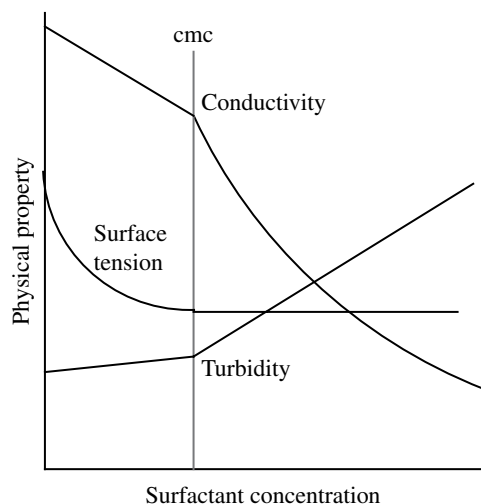
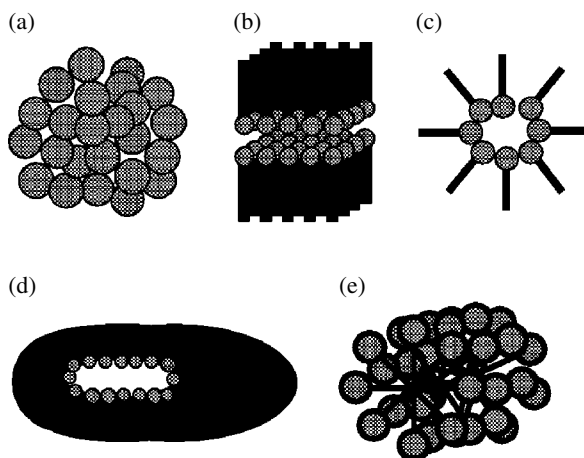


Figure 6.5 Some important manifestations of micelle formation: abrupt changes in solution conductivity, a discontinuity in the surface tension/concentration curve, and a sudden increase in solution turbidity.

Figure 6.6 Five of the proposed micelle shapes, as interpreted from experimental data: (a) spherical, (b) lamellar, (c) inverted (or reversed), (d) disk, and (e) cylindrical or rodlike.



equivalent conductivity (top curve), the break may be associated with an increase in the mass per unit charge of the conducting species. For light scattering (bottom curve), the change in solution turbidity indicates the appearance of a scattering species of significantly greater size than the monomeric solute. These and many other types of measurement serve as evidence for the formation of aggregates or micelles in solutions of surfactants at relatively well-defined concentrations.

In 1920 it was reported that the osmotic activity of solutions of potassium stearate indicated the presence of a considerable degree of aggregation and suggested that the aggregated species should be termed micelles. To explain both the osmotic data and corresponding changes in conductance, it was suggested that two distinct types of micelle were being formed, a spherical species composed of ionized salt molecules and a nonionic lamellar aggregate structure involving unionized acid molecules (Figure 6.6a, b). Subsequent interpretations of the results of such studies were made in terms of a single type of structure. The single structure or Hartley model called for essentially spherical micelles with a diameter equal to approximately twice the length of the hydrocarbon chain. A similar “reversed” or “inverted” spherical micelle for nonaqueous systems is illustrated in Figure 6.6c for completeness. It was suggested that the structure was composed of 50–100 molecules and that the association should occur over a relatively narrow concentration range. The interior of the micelle (Figure 6.6a) was described as being essentially hydrocarbon in nature, while the surface consisted of the charged head groups. The close proximity of the head groups required that some fraction be tightly bound to their counterions, thereby reducing repulsions between neighbors and reducing the overall mobility of the aggregated species in an electric field. The classical Hartley micelle successfully described the characteristics of many, if not all, surfactant systems and achieved a deservedly honored place in the history of surface and colloid science. Other proposed structures are illustrated in Figure 6.6d and e. More recent modifications to the basic micellar model have served to fill in the fine points but have not significantly changed the basic picture of micellar structures.

Early discussions of the micellization phenomenon emphasized that the “dislike” of the hydrophobic portion of a surfactant molecule for water was not a repulsive interaction, but rather an attractive preference of water for water and hydrocarbon for hydrocarbon. It was not suggested that there existed a particularly strong attraction among the hydrophobic chains in the molecules, since their interactions are nonpolar and, therefore, relatively small. That idea was reflected in the low melting and boiling points of hydrocarbons relative to polar materials of similar or lower

molecular weight. Because of its chemical nature, however, water possesses a very strong cohesive force, which results in many of its unusual properties.

When a molecule containing both a hydrophobic group and a hydrophilic group is introduced into water, a distortion of the water structure to accommodate the solute molecules occurs, disrupting the happy accommodation of the water molecules and requiring them to orient around the hydrophobic tail in a more icelike structure. That more structured arrangement increases the free energy (basically the entropy) of the system. The physical result of such an energy increase is a tendency for the surfactant molecules to adsorb at available interfaces where preferred molecular orientations may serve to reduce the total free energy of the solution or for the formation of molecular aggregates with their hydrophobic portions directed toward the interior of the micelle. Micellization, therefore, is an alternative mechanism to adsorption for the reduction of solution free energy by the minimization of the distortion of the structure of the bulk water. Although the removal of the hydrophobe from the water environment results in a decrease in energy, the adsorbed or aggregated hydrophobe may experience a loss of freedom (decrease in entropy) that would thermodynamically reduce the attractiveness of the process. In this case, the water wins out, overall.

It must also be remembered that the surfactant molecule also possesses a hydrophilic group, the interaction of which with the water may decrease the free energy of the system. The partial removal of that group from the solution through adsorption or micelle formation can result in an increase in free energy. Additionally, the hydrophilic group may possess an electrostatic charge so that the process of adsorption or micellization can introduce electrostatic repulsions, which act to inhibit the removal of the molecule from solution. The situation, then, becomes a tug-of-war between the opposing free energy considerations. The occurrence of micellization in a given surfactant system, and the concentration at which micelle formation occurs, will therefore be determined by the relative balance of the forces favoring and retarding the molecular aggregation process. Since the magnitudes of the opposing forces are determined by the chemical compositions of the solute molecules, where all other aspects (temperature, pressure, solvent, etc.) are held constant, it is the chemical constitution of the surface-active species that ultimately controls events. It should be possible, then, to make reasonable generalizations about the micellization characteristics of surfactants and their chemical structures.

Using the Hartley concept as a starting model, modern studies using techniques unimagined by the earlier workers have produced more detailed pictures of the submicroscopic nature of micelles. Micelles, of course, are not static species. They are very dynamic in that there is a constant, rapid interchange of molecules between the aggregates and the solution phase. It is also reasonable to assume that surfactant molecules do not pack into a micelle in such an orderly manner as to produce a smooth, uniform surface structure. If one could photograph a micelle with ultrahigh-speed film, freezing the motion of the molecules, the picture would almost certainly show an irregular molecular cluster more closely resembling a cocklebur than a golf ball.

The simplicity of the Hartley micelle has left it open to criticism, since it fails to adequately explain many experimentally observed phenomena. Models of micelles have been suggested that appear to differ substantially from those of Hartley. Particularly significant differences are a much greater degree of penetration of water into the micelle interior and a relatively smaller interior or core radius. Some of those models appear to better explain some of the solubilization data for hydrophobic additives and the measured or inferred micro-viscosities of micellar interiors. They have also been used to better explain some results in micelle-catalyzed reactions. The various models of micelles are, of course, just that – models that assist the investigator to visualize what may be occurring in a surfactant solution to produce the observed experimental results.

The relationship of models to reality may be questionable, but their utility as “tools of the trade” is quite real.

Although the classical picture of a micelle is that of a sphere, most evidence indicates that spherical micelles are not the rule and may in fact be the exception. As a result of geometric packing requirements and analyses (to be discussed below), ellipsoidal, disk-shaped, and rodlike structures may be the more commonly encountered shapes. However, from the standpoint of providing a concept of micelles and micelle formation for the nonspecialist, the Hartley spherical model remains a useful and meaningful tool.

6.3.2 Thermodynamics of Dilute Surfactant Solutions

It is unlikely that a single “theory of everything” for the aggregation of surfactant molecules into micelles or other structures will be developed soon, given the great diversity in molecular compositions available today. It is something like models for predicting the weather – we have a pretty good grasp of what is going on in general terms, but when we throw in a seemingly small variation (like the famous fluttering butterfly in China, for example), things can rapidly begin to fall apart. Such models may “predict” the global weather 50 or 100 years hence, but we still do not know for sure if it will rain 3 days from now! While classical approaches based on phase separation and mass action models have proven extremely useful, they do not possess adequate flexibility to extend their utility to explain such phenomena as the existence of cylindrical micelles, vesicles, and bilayer structures. In particular, they have not been able to theoretically quantify the role played by molecular geometry in predicting the shapes and structures that may result from a given molecular architecture.

In attempting to devise a comprehensive theory for micelle formation, there are two possible approaches. One may, if so inclined, begin with basic statistical mechanics, considering complex interactions between surfactant molecules and water, as well as solute–solute and solvent–solvent interactions. However, since the fundamental principles of the hydrophobic interactions between small molecules in water are still not clearly defined, there seems to be little hope that such an approach will produce a satisfactory result. However, even if a theoretically satisfying model did result, the mathematical complexities would possibly obscure any clear insight based upon chemical realities.

Occupying the other end of the theoretical spectrum are approaches that ignore the statistical mechanical details in favor of an overall thermodynamic understanding. Pure thermodynamics, however, tends to be somewhat obscure (to those not skilled in the art) and must eventually fall back on some aspects of molecular interactions to validate its conclusions. Whatever favorite theory an author may champion, in order to be useful, it must not only be able to explain experimental observations, but it must also successfully predict as yet unobserved phenomena – as does any valid scientific theory. If too many unknown or variable parameters are included, theory tends to become a numerical game, an exercise in curve fitting that may lose its predictive capacity and credibility.

On the other hand, a theoretical assumption may start out as an acceptable or comfortable explanation of experimental data, but if the “truth” of that assumption cannot be tested or if its shortcomings are not obvious, it may be promoted to the rank of being an article of faith causing contradictory data to be discarded or relegated to a category of “bad” experimental technique. In the absence of a firm basis for choosing one approach to the theory of micelle formation, or any other theory for that matter, over others, and in line with the stated goal of keeping things as simple as possible, the following discussion is limited to a brief summary of the classical concepts of micelle formation.

6.3.3 Classical Theories of Micelle Formation

In the literature on micelle formation, two primary models have gained general acceptance as useful (although not necessarily exact) for understanding the energetic basis of the process. The two approaches are the mass action model, in which the micelles and monomeric species are considered to be in a kind of chemical equilibrium, and the phase separation model, in which the micelles are considered to constitute a new phase formed in the system at and above the critical micelle concentration. In each case, classical thermodynamic approaches are used to describe the overall process of micellization.

In the mass action model, it is assumed that equilibrium exists between the monomeric surfactant and the micelles. For the case of nonionic (or unionized) surfactants, the monomer–micelle equilibrium can be written as



with a corresponding equilibrium constant, K_m , given by

$$K_m = [S_n] / [S]_n \quad (6.2)$$

where brackets indicate molar concentrations and n is the number of monomers in the micelle or the aggregation number. Theoretically, one must use activities rather than concentrations in Eq. (6.2); however, the substitution of concentrations for activities is generally justified by the fact that the **cmc** occurs at such low concentrations that activity coefficients can be assumed to be unity.

It is usually observed that the **cmc** for a surfactant is relatively sharp and characteristic of a given material. Although the detailed theory of micelle formation can become quite complex, the sharpness of the **cmc** can be explained conceptually in terms of the law of mass action. If C_t denotes the total concentration of surfactant in solution, C_m the fraction of monomer units in the aggregated or micellar state, and C_s that of free molecules, Eq. (6.22) may be written as

$$K_m = C_m / (nC_t^n) \quad (6.3)$$

In the process of micelle formation, there will be some value of C , C_{eq} , at which the number of surfactant molecules in the micellar form will be equal to that in the form of free surfactant molecules. At that concentration, $C_m = C_t = C_{eq}/2$. Using Eq. (6.3), one can then write

$$K_m = (1/n) \left(\frac{1}{2} C_{eq} \right)^{-(n-1)} \quad (6.4)$$

At any value of C_t , the relationship between C_s and C_m can be found by substitution of Eq. (6.4) into Eq. (6.2):

$$C_m / (C_s)_n = (C_{eq}/2)^{-(n-1)} \quad (6.5)$$

where $C_t = C_s + C_m$. Rearrangement of Eq. (6.5) gives

$$C_m / C_{eq} = \frac{1}{2} \left(2C_s / C_{eq} \right)_n \quad (6.6)$$

Using Eq. (6.6) as a starting point, one can estimate how the individual concentrations vary in the area of $C_t = C_{eq}$ for a given aggregation number, n . Aggregation numbers for many surfactants

lie in the range of 50–100; Table 6.2 gives the percentages of molecules in the associated state for $n = 50, 75$, and 100 , calculated according to Eq. (6.6). The results indicate that, while the **cmc** for a given system may not represent a truly sharp change in conditions, once the formation of micelles has begun, any increase in surfactant concentration will be directed almost completely to the formation of more micelles. It is also obvious that the larger the aggregation number for a given system, the sharper will be the transition from monomolecular solution to predominantly micelles.

Table 6.2 Percentage of total surfactant molecules in micellar form near $C_s = C_{eq}$ calculated according to Eq. (6.6).

The alternative approach to modeling micelle formation is to think in terms of a phase separation model in which, at the **cmc**, the concentration of the free surfactant molecules becomes constant (like a solubility limit or K_{sp}), and all additional molecules go into the formation of micelles. Analysis of the two approaches produces the same general result in terms of the energetic balance of micelle formation (with some slight differences in detail), so the choice of model is really a matter of preference and circumstances. There is evidence that the activity of free surfactant molecules does increase above the **cmc**, which tends to support the mass action model; however, for most purposes, that detail is of little consequence.

6.3.4 Free Energy of Micellization

Using Eq. (6.2) as a basis, the standard free energy for micelle formation per mole of micelles is given by

$$\Delta G_m^\circ = -RT \ln K_m = -RT \ln S_n + nRT \ln S \quad (6.7)$$

while the standard free energy change per mole of free surfactant is

$$\Delta G_m^\circ / n = -(RT / n) \ln S_n + RT \ln S \quad (6.8)$$

Table 6.2 Percentage of total surfactant molecules in micellar form near $C_s = C_{eq}$ calculated according to Eq. (6.6).

C_s/C_{eq}	% C_t in micellar form		
	$n = 50$	$n = 75$	$n = 100$
0.45	0.57	0.04	0.003
0.47	4.6	1.01	0.22
0.49	27	18	12
0.495	38	32	27
0.50	50	50	50
0.505	62	68	73
0.51	73	81	88
0.52	87	95	98
0.53	95	99	99.7
0.54	98	99.7	99.95
0.55	99.1	99.9	99.99

As shown above, at (or near) the **cmc** $S \approx S_n$, so the first term on the right side of Eq. (6.8) can be neglected, and an approximate expression for the free energy of micellization per mole of surfactant will be

$$\Delta G_m^\circ = RT \ln \text{cmc} \quad (6.9)$$

The situation is complicated somewhat in the case of ionized surfactants because the presence of the counterion and its degree of association with the monomer and micelle must be taken into consideration. For an ionic surfactant, the mass action equation would be

$$nS_x + (n - m)C_y \leftrightarrow S_n m(x) \quad (6.10)$$

The degree of dissociation of the surfactant molecules in the micelle, α , the micellar charge, is given by $\alpha = m/n$. The ionic equivalent to Eq. (6.2) would then be

$$K_m = [S_n] / [S_x]_n [C_y]^{n-m} \quad (6.11)$$

where m is the concentration of free counterions, C (e.g. those not bound to the micelle). The standard free energy of micelle formation will be

$$\Delta G_m^\circ = (RT/n) \{ n \ln [S_x] + (n - m) \ln [C_y] - \ln [S_n] \} \quad (6.12)$$

At the **cmc** $[S^{-(+)}] = [C^{+(-)}] = \text{cmc}$ for a fully ionized surfactant, and Eq. (6.12) can be approximated as

$$\Delta G_m^\circ = RT \left[1 + (m/n) \right] \ln \text{cmc} \quad (6.13)$$

When the ionic micelle is in a solution of high electrolyte content, the situation described by Eq. (6.12) reverts to the simple nonionic case given by Eq. (6.9).

In general, but not always, micelle formation is found to be an exothermic process, favored by a decrease in temperature. The enthalpy of micellization, ΔH_m , given by

$$-\Delta H_m = RT^2 \left[d \ln \text{cmc} / dT \right] \quad (6.14)$$

may therefore be either positive or negative, depending on the system and conditions. The process, however, always has a substantial positive entropic contribution to overcome any positive enthalpy term, so micelle formation is primarily an entropy-driven process.

More elaborate models employ more complicated mathematical treatments with more rigorous statements of the physical phenomena involved. However, they yield little information of value as far as understanding a given practical system is concerned. A different, and perhaps more conceptually useful, approach emphasizes the importance of molecular geometry in defining the characteristics of an aggregating system. Such a geometrical approach would seem to be especially useful for applications in which the chemical structure of the surfactant is of central importance.

6.4 Molecular Geometry and the Formation of Association Colloids

The theoretical developments based upon the effects of geometry on molecular aggregation have shown that physical characteristics of surfactants such as **cmc**, aggregate size and shape, and micellar size distribution (polydispersity) can be quantitatively described without relying on a

detailed knowledge of the specific energetic components of the various molecular interactions. It is also useful in that it applies equally well to micelles, vesicles, and bilayer membranes, the latter lying outside the normal models of association processes. For that reason, the geometrical approach warrants a somewhat closer look.

The classical picture of micelles formed by simple surfactant systems in aqueous solution is that of a sphere with a core of essentially liquid-like hydrocarbon surrounded by a shell containing the hydrophilic head groups along with associated counterions, water of hydration, etc. Regardless of any controversy surrounding the model, it is usually assumed that there are no water molecules included in the micellar core, since the driving force for micelle formation is a reduction of water–hydrocarbon contacts. Water will, however, be closely associated with the micellar surface; as a result, some water–core contact must occur at or near the supposed boundary between the two regions. The extent of that water–hydrocarbon contact will be determined by the surface area occupied by each head group and the radius of the core. It seems clear from a conceptual viewpoint that the relative ratio between the micellar core volume and surface area must play an important role in controlling the thermodynamics and architecture of the association process. Equally important is the need to understand the constraints that such molecular geometry places on the ability of surfactants to pack during the aggregation process to produce micelles, microemulsions, vesicles, and bilayers.

Israelachvili (see Bibliography) and others have shown that the geometric factors that control the packing of surfactants and lipids into aggregated structures can be conveniently given by what is termed a “critical packing parameter” or shape factor given by v/a_0l_c , where v is the volume of the hydrophobic portion of the molecule, a_0 is the optimum head group area, and l_c is the critical length of the hydrophobic tail, effectively the maximum extent to which the chain can be stretched under the specific conditions imposed by molecular structure, environment, etc. The value of the packing parameter will determine the type of association structure formed in each case. A summary of some of the structures to be expected from molecules falling into various “critical packing” categories is given in Table 6.3.

While examples almost surely will be found of materials that do not fit neatly into such a scheme, the general concepts are usually valid. For surfactants and other amphiphilic materials that form

Table 6.3 Expected aggregate characteristics in relation to surfactant critical packing parameter, v/a_0l_c .

Critical packing parameter	General surfactant type	Expected aggregate structure
<0.33	Simple surfactants with single chains and relatively large head groups	Spherical or ellipsoidal micelles
0.33–0.5	Simple surfactants with relatively small head groups, or ionic surfactants in the presence of large amounts of electrolyte	Relatively large cylindrical or rod-shaped micelles
0.5–1.0	Double-chain surfactants with large head groups and flexible chains	Vesicles and flexible bilayer structures
1.0	Double-chain surfactants with small head groups or rigid, immobile chains	Planar extended bilayer structures
>1.0	Double-chain surfactants with small head groups, very large, bulky hydrophobic groups	Reversed or inverted micelles

bilayer structures, Israelachvili has offered several generalizations that make it easier to understand the geometric consequences of the surfactant structure:

- 1) Molecules with relatively small head groups, and therefore large values for $\mathbf{v}/\mathbf{a}_0\mathbf{l}_c$, will normally form extended bilayers, large (low curvature) vesicles, or inverted micellar structures. Such structures can be created in anionic systems by changes in pH, high salt concentrations, or the addition of multivalent cations, especially Ca^{2+} .
- 2) Molecules containing unsaturated hydrocarbon chains, especially multiple *cis*-double bonds, will have smaller values for \mathbf{l}_c and thus will tend toward the formation of larger vesicles or inverted structures.
- 3) Multichained molecules held above the melting temperature of the hydrocarbon chain may undergo increased chain motion, allowing *trans*-gauche chain isomerization, reducing the effective value of \mathbf{l}_c , and resulting in changes in aggregate structures. This effect may be of particular importance in understanding the effects of temperature on biological membranes.

The foregoing generalizations on bilayer assemblies of surfactants and other amphiphilic molecules offer a broad view of the types of structure that may be formed as a result of the self-assembly process. They consider only the fundamental relationships between structure and the geometric characteristics of the molecules involved. Not considered are any effects on the systems that may exist because of curvature or other distortions of the molecular packing. The interested reader can obtain more in-depth discussions in the works of Israelachvili and Fendler cited in the Bibliography. The unique characteristics of the bilayer and vesicle assemblies have attracted the attention of scientists in many disciplines for both theoretical and practical reasons. The following brief discussion skims the surface of what is sure to become an even more interesting and important area of surfactant-related surface science.

Although it is convenient to visualize the micellar core as a bulk hydrocarbon phase, the density may not be equal to that of the analogous true bulk material. X-ray evidence indicates that the molecular volumes of surfactants in micelles are essentially unchanged by the aggregation process. If a molecular volume for a hydrocarbon chain in the micellar core equal to that of a normal hydrocarbon is assumed, the core volume, \mathbf{v} , can be calculated from

$$\mathbf{v} = \mathbf{n}'(27.4 + 26.9\mathbf{n}'_c) \times 10^{-3} (\text{nm}^3) \quad (6.15)$$

where \mathbf{n}' is an effective micellar aggregation number and \mathbf{n}'_c is the number of carbon atoms per chain in the core. In general, the value of \mathbf{n}'_c will be one less than the total number of carbons in the hydrocarbon chain, \mathbf{n}_c , since the first carbon after the head group is highly solvated and may be considered to be a part of it. For “normal” surfactants with a single hydrocarbon tail, \mathbf{n}' will be equal to the aggregation number, \mathbf{n} , while for those that possess a double tail, $\mathbf{n}' = 2\mathbf{n}$.

If one assumes that the micellar core has no “hole” at its center, one dimension of the aggregate species will be limited by the length of the hydrocarbon chain when extended to its fullest. That maximum length can be calculated by assuming a distance of 0.253 nm between alternate carbon atoms of the extended hydrocarbon chain and adding the value of the van der Waals radius of the terminal methyl group (≈ 0.21 nm) and half the bond distance between the first carbon in the core and that bonded to the head group (≈ 0.06 nm). The maximum extended length \mathbf{l}_{max} for a normal hydrocarbon chain with \mathbf{n}'_c core carbon atoms, therefore, is given by

$$\mathbf{l}_{\text{max}} = 0.15 + 0.1265\mathbf{n}'_c \text{ nm} \quad (6.16)$$

Since hydrocarbon chains in the liquid state are never fully extended, a dimension, l_{eff} , can be defined that gives the statistically most likely extension as calculated by the same procedure used for the calculation of polymer chain dimensions. For a chain with $n'_c = 11$, the ratio of l_{max} to l_{eff} will be approximately 0.75. In the micellar core, due to restrictions imposed by the attachment of the hydrocarbon tail to the head group bound at the surface, the mobility of the chains may be significantly limited relative to that of bulk hydrocarbon chains. The presence of “kinks” or gauche chain conformations, which may be imposed by packing considerations, will result in a calculated l_{max} amounting to only about 80% of the theoretical maximum.

Since hydrocarbon chains possess restricted bond angles as well as bond lengths, additional restrictions on the maximum extension of the chain arise beyond those mentioned previously. Chain segments located at the transition region from core to shell, for example, cannot assume arbitrary conformations in order to produce a perfectly smooth surface. The micellar surface, therefore, must be assumed to be rough or irregular, although the dynamic nature of the aggregate may obscure any practical effect of such roughness.

A number of researchers have considered in detail some of the geometric restrictions that govern micelle sizes, shapes, and size dispersity. Their analysis of the geometrical and thermodynamic factors appears to allow for the prediction of most aspects of the aggregation of surface active molecular species, including the **cmc**, average aggregation number, polydispersity of micelle sizes, and the most likely shape of the aggregated species.

Although the geometric approach shows great promise, it has not worked its way into the general thinking on micelles. It is, however, finding wide acceptance in areas related to biological membranes and aggregates. It can be expected that as more experimental data can be correlated with the predictions of geometric considerations, such an approach will gain ground as a basis for the design of surfactant molecules with specific desirable aggregation characteristics. With the preceding concepts in mind, we now turn to some of the experimental results that have helped bring us to our current state of understanding of surfactant aggregation or micelle formation.

6.5 Experimental Observations of Micellar Systems

The preceding sections presented a brief review of some of the basic theoretical concepts pertaining to the formation of surfactant micelles. The following sections are devoted to the presentation of some experimental results from the literature that illustrate many of the various effects of surfactant chemical structure and solution environment on the aggregation process. While the previously described models of micelle formation serve as a useful basis for the interpretation of the results given below, it must be remembered that in all cases they represent a very simplified picture and involve a number of assumptions, many of which are not fully justified by experiment.

6.5.1 Micellar Aggregation Numbers

Several references have been made to the number of surfactant monomers aggregating to form a micelle – the aggregation number, n . The classical method for determining n is to use elastic light scattering. It is possible to determine a weight-average molecular weight (M_w) for a micellar solution, and therefore the average number of surfactant molecules in the structure, from the intensity of light scattered at a given angle at surfactant concentrations above the **cmc** relative to that of the pure solvent (or solvent plus surfactant below the **cmc**). Newer techniques such as laser light

scattering and fluorescence quenching produce data that allow for the determination of the aggregation number and the distribution of micellar sizes, as well as giving some idea of their approximate shapes. Typical aggregation numbers for various surfactant types are given in Table 6.4.

Because the size and size distribution of micelles are sensitive to many internal (hydrophobic structure, head group type, etc.) and external (temperature, pressure, pH, electrolyte content, etc.) factors, it is sometimes difficult to place too much significance on reported values of n . However, some generalizations can be made that are usually found to be true. They include the following:

- 1) In aqueous solutions, it is generally observed that the greater the length of the hydrophobic chain of a homologous series of surfactants, the larger will be the aggregation number, n .
- 2) A similar increase in n is seen when there is a decrease in the “hydrophilicity” of the head group – for example, a higher degree of ion binding for an ionic surfactant or a shorter polyoxyethylene chain in a typical nonionic material.
- 3) External factors that result in a reduction in the “hydrophilicity” of the head group such as high electrolyte concentrations will also cause an increase in the aggregation number.
- 4) Changes in temperature will affect nonionic and ionic surfactants differently. In general, higher temperatures will result in small decreases in aggregation numbers for ionic surfactants but significantly large increases for nonionic materials. The effect on nonionic surfactants is related to the cloud point phenomenon discussed previously.
- 5) The addition of small amounts of non-surfactant organic materials of low water solubility will often produce an apparent increase in micelle size, although that may be more an effect of solubilization (see Chapter 8) than an actual increase in the number of surfactant molecules present in the micelle.

While the question of the size of micelles is of great theoretical interest, it is not usually very significant (as far as we know) in most surfactant applications. Of more general importance is the concentration at which micelle formation occurs, the critical micelle concentration, since it is then when many of the most useful surfactant properties come into play.

Table 6.4 Aggregation numbers for some surfactants in water.

Surfactant	Temperature (°C)	Aggregation number
$C_{10}H_{21}SO_3^- Na^+$	30	40
$C_{12}H_{25}SO_3^- Na^+$	40	54
$(C_{12}H_{25}SO_3^-)_2Mg^{2+}$	60	107
$C_{12}H_{25}SO_4^- Na^+$	23	71
$C_{14}H_{29}SO_3^- Na^+$	60	80
$C_{12}H_{25}N(CH_3)_3^+ Br^-$	23	50
$C_8H_{17}O(CH_2CH_2O)_6H$	30	41
$C_{10}H_{21}O(CH_2CH_2O)_6H$	35	260
$C_{12}H_{25}O(CH_2CH_2O)_6H$	15	140
$C_{12}H_{25}O(CH_2CH_2O)_6H$	25	400
$C_{12}H_{25}O(CH_2CH_2O)_6H$	35	1400
$C_{14}H_{29}O(CH_2CH_2O)_6H$	35	7500

6.5.2 The Critical Micelle Concentration

Because many factors have been shown to strongly affect the observed critical micelle concentration of surfactant systems, the following discussion is divided to isolate (as much as possible) the various important components, including the nature of the hydrophobic tail, the head group type, including counterion, and the role of external factors not directly related to the chemical structure of the surfactant.

There are a number of relatively easy (with practice) experimental methods for determining the **cmc** of a surfactant. One compendium, for instance, contains 71 possibilities, along with a critical discussion of each. The method of choice will depend on the availability of the various techniques, the relationship between the technique and the ultimate application, and the personal preferences of the investigator.

Because of uncertainties in micellar thermodynamics and the nature of micellar species, each procedure for the determination of critical micelle concentrations will carry with it the need to make a somewhat arbitrary decision as to the exact value to be reported. The chosen value may depend on the way in which the data are plotted, and lines are extrapolated, the characteristics of the measurements, the specific techniques (and care) used in the procedure, the accuracy of experimental controls, the judgment of the investigator, etc. Light scattering measurements, for example, can be used to determine the **cmc** and yield a value related to the weight-average molecular weight, the size of the micelle, and even some shape factor. An older technique such as dye solubilization, on the other hand, will produce a number-average value that will always be smaller than the corresponding weight average for a polydisperse system. In addition, procedures such as the use of dyes introduce foreign materials that may actually alter the thermodynamics of the system through molecular interactions with the surfactant, so even the choice of dye may influence the results. Even time-honored techniques that measure some physical characteristic of the solution such as surface tension and conductivity will often produce results differing in numerical value, if not order of magnitude.

It is obvious, therefore, that any discussion of **cmc** data must be tempered with the knowledge that the reported values must not be taken to be absolute; rather, they reflect certain variable factors inherent in the procedures employed for their determination. The variations found for nominally the same material under supposedly identical conditions in the literature should be accepted as minor “noise” that does not significantly affect the overall picture of the system. With those caveats in mind, our attention now turns to some of the trends that have been identified over the years that relate surfactant critical micelle concentrations to molecular structures.

6.5.3 The Hydrophobic Group

The length of the chain of a hydrocarbon surfactant has been shown to be a major factor determining its **cmc**. It is known that the **cmc** decreases logarithmically as the number of carbons in the chain of a homologous series n_c increases. For straight-chain hydrocarbon surfactants of 16 carbon atoms or less bound to a single terminal head group, the **cmc** is usually reduced by approximately one half with the addition of each $-\text{CH}_2-$ group. For nonionic surfactants, the effect can be much larger, with a decrease by a factor of 10 following the addition of two carbons to the chain. The insertion of a phenyl and other linking group, the branching of the alkyl group, and the presence of a polar substituent group on the hydrophobic chain can produce different effects on the **cmc**, as discussed below. For now, we confine the subject to simple alkyl hydrophobic groups.

Mathematically, the relationship between the hydrocarbon chain length and **cmc** can be expressed by the so-called Klevens constant as

$$\log_{10} \text{cmc} = \mathbf{A} - \mathbf{B}n_c \quad (6.17)$$

where **A** and **B** are constants specific to the homologous series under constant conditions of temperature, pressure, etc. Values of **A** and **B** for a wide variety of surfactant types have been determined, and some are listed in Table 6.5. It has generally been found that the value of **A** is approximately constant for a particular ionic head group, while **B** is constant and approximately equal to $\log_{10} 2$ for all paraffin chain salts having a single ionic head group. The value of **B** will change, however, in systems having two head groups, or for nonionic systems.

A number of empirical relationships between **cmc** and hydrocarbon chain length consistent with the relationship in Eq. (6.17) have been developed by various researchers. The fundamental principle on which the derivations are based stems from the fact that the **cmc** is related to the free energy change on micelle formation through Eqs. (6.13) and (6.14). Rearrangement of Eq. (6.13) yields

$$\ln \text{cmc} = \Delta G_m / RT + \ln 55.4 \quad (6.18)$$

Converting to \log_{10} gives

$$\log_{10} \text{cmc} = \Delta G_m / 2.3RT + \log_{10} 55.4 \quad (6.19)$$

Because the aggregation process represents a balance of the forces tending to favor micelle formation and those in opposition, the free energy term can be divided into its components as

$$\Delta G_m = \Delta G_m^h + \Delta G_m^w \quad (6.20)$$

where the superscripts **h** and **w** indicate the hydrophobic forces driving the system to aggregation and the work required to bring the hydrophilic head groups into close proximity at the micellar surface, respectively. Data on the solubility of hydrocarbons in water indicate that the contribution

Table 6.5 Klevens constants (Eq. (6.17)) for common surfactant classes.

Surfactant class	Temperature (°C)	A	B
Carboxylate soaps (Na ⁺)	20	1.85	0.30
Carboxylate soaps (K ⁺)	25	1.92	0.29
<i>n</i> -Alkyl-1-sulfates (Na ⁺)	45	1.42	0.30
<i>n</i> -Alkyl-2-sulfates (Na ⁺)	55	1.28	0.27
<i>n</i> -Alkyl-1-sulfonates	40	1.59	0.29
<i>p</i> - <i>n</i> -Alkylbenzene sulfonates	55	1.68	0.29
<i>n</i> -Alkylammonium chlorides	25	1.25	0.27
<i>n</i> -Alkyltrimethylammonium bromides	25	1.72	0.30
<i>n</i> -Alkylpyridinium bromides	30	1.72	0.31

to ΔG_m^h of each $-\text{CH}_2-$ group added to the chain is a constant. In addition, the contribution of the terminal $-\text{CH}_3$ differs only by the addition of a constant \mathbf{K} , so

$$\log_{10} \text{cmc} = \Delta G_m^w / 2.3RT + n_c (\Delta G_m^h / 2.3RT) + \mathbf{K}' \quad (6.21)$$

where

$$\mathbf{K}' = \log_{10} + \mathbf{K} / 2.3RT \quad (6.22)$$

and n_c is the number of carbon atoms in the hydrocarbon tail. If it is assumed that the contribution of the head group, ΔG_m^w , is independent of n_c , then for a homologous series Eq. (6.21) can be abbreviated in the form of Eq. (6.17) where

$$\mathbf{A} = \Delta G_m^w / 2.3RT + \mathbf{K}' \quad (6.23a)$$

and

$$\mathbf{B} = -\Delta G_m^h / 2.3RT \quad (6.23b)$$

It is apparent that such an analysis qualitatively describes the empirical observations related to the fact that the constant \mathbf{A} is relatively invariable for a given head group and \mathbf{B} shows only small changes in different homologous series of ionic surfactants.

For nonionic surfactants, in the absence of electrical contributions to the aggregation process, the relative importance of the tail and head groups to the system changes. An empirical relationship between the **cmc** and the number of oxyethylene $(\text{OE})_y$ groups in several nonionic surfactants series has the form

$$\ln \text{cmc} = \mathbf{A}' + \mathbf{B}'y \quad (6.24)$$

where \mathbf{A}' and \mathbf{B}' are constants related to a given hydrophobic group. Examples of \mathbf{A}' and \mathbf{B}' for several commonly encountered hydrophobic groups are given in Table 6.6. In each case, the results are for one temperature and can be expected to vary significantly, given the known sensitivity of such systems to changes in \mathbf{T} . In all the cases, not surprisingly, the **cmc** is found to decrease as the hydrophobicity of the molecule increases.

Most of the ionic surfactants investigated have been of the simple 1 : 1 electrolyte type. With the appearance of surfactants with two or three ionic groups at one end of the hydrocarbon tail, it has become of interest to determine the **cmc**-related consequences of such structures. A number of

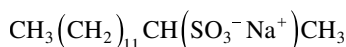
Table 6.6 Empirical constants relating **cmc** and OE content for various hydrophobic groups in nonionic surfactants (Eq. (6.24)).

Hydrophobic group	\mathbf{A}	\mathbf{B}
$\text{C}_{12}\text{H}_{25}\text{O}-$	3.60	0.048
$\text{C}_{13}\text{H}_{27}\text{O}-$	3.59	0.091
$\text{C}_{18}\text{H}_{35}\text{O}-$ (oleyl)	3.67	0.015
$\text{C}_{18}\text{H}_{37}\text{O}-$ (stearyl)	2.97	0.070
$\text{C}_9\text{H}_{19}\text{C}_6\text{H}_4\text{O}-$	3.49	0.065

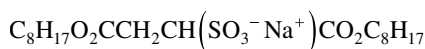
Table 6.7 The critical micelle concentrations of some surfactants having two or more ionic groups compared, where possible, with that of the corresponding fatty acid.

Surfactant (R = <i>n</i> -Alkyl)	cmc (mM)	Ratio of cmc's (for corresponding fatty acid)
R ₈ CH(COOK) ₂	350	3.5
R ₁₀ CH(COOK) ₂	130	5.2
R ₁₂ CH(COOK) ₂	48	7.7
R ₁₄ CH(COOK) ₂	17	10
R ₁₆ CH(COOK) ₂	6.3	≈15
R ₁₂ CH(SO ₃ H)(COOH)	2.4	—
R ₁₄ CH(SO ₃ H)(COOH)	0.6	—
R ₁₄ CH(SO ₃ Na)COOCH ₂ CH ₂ SO ₃ Na	8.0	—
R ₁₆ CH(SO ₃ Na)COOCH ₂ CH ₂ SO ₃ Na	2.5	—

studies of materials such as α -sulfonated fatty acids and their esters, alkyl malonates, and alkyl tricarbonylates exhibit a linear relationship similar to Eq. (6.17). Such surfactants have generally been found to have a lower Krafft point than the corresponding surfactant with a single head group. Because of the large size of the head group, members of these classes of materials exhibit other properties significantly different from those of more common surfactants of similar characteristics. A comparison of the **cmc**'s of alkyl malonates with those of the corresponding fatty acid indicates that the extra head group produces a large increase in the **cmc** (Table 6.7). The difference results mainly from the larger electrical contribution to the thermodynamics of micelle formation. If, instead of a simple straight hydrophobic tail, a surfactant has a branched structure, with the head group attached at some point other than the terminal carbon, as for instance, in sodium tetradecane-2-sulfonate



or if there are two independently attached hydrophobes as in the diesters of sulfosuccinates



the aggregation process can be expected to differ from that of normal hydrocarbon surfactants.

When the hydrophobe is branched, the additional carbon atoms off the main chain contribute a factor equivalent to about half that for a main chain carbon. The critical micelle concentrations of a series of sodium alkyl sulfates in which the total number of carbon atoms ranged from 8 to 18 and the position of the sulfate substitution changed from the terminal to the middle carbons are listed in Table 6.8. The data show that, except for the lower carbon number samples, the homologous series follows a linear relationship similar to the Klevens equation.

The values of the constants **A** and **B** for the different series are given in Table 6.9. From the data it can be seen that the value of **A** decreases slightly as the sulfate group is moved toward the interior of the hydrocarbon chain. Such an effect may be interpreted as indicating a smaller thermodynamic contribution to micelle formation from added methylene groups with internal sulfation. The values of **B** remain relatively constant within a series with different sulfate locations. For a series of alkyl sulfates with the same number of carbon atoms, the **cmc** increases as the sulfate

Table 6.8 The effect of sulfate substitution and total carbon content on the **cmc**'s of sodium alkyl sulfates at 40 °C.

Total carbon number	Sulfate position	cmc (mM)
8	1	136
8	2	180
10	2	49.5
11	3	28.9
11	6	83
14	1	2.4
14	2	3.3
14	3	4.3
14	4	5.15
14	5	6.75
14	7	9.70
15	2	1.71
15	3	2.20
15	5	3.4
15	8	6.65
16	1	5.8
16	4	1.72
16	6	2.35
16	8	4.25
18	1	1.65
18	2	2.6
18	4	4.5
18	6	7.2

group is moved internally. In the example of sodium tetradecyl sulfate, the measured **cmc** varies from 9.7 mM for the 7-sulfate to 2.4 mM for the terminal sulfate. By analogy to straight-chain sulfates, such a change would correspond to a decrease of about two carbon atoms.

Many surfactants of commercial interest have nonterminal hydrophilic substitution. However, because such materials are not usually of sufficient purity to warrant detailed thermodynamic analysis, extensive micellization data have not been reported. The effects of other types of branching and hydrophobic substitution on the micellization of 2-*n*-alkylbenzene sulfonates have been reported. Other reports have dealt with the **cmc**'s of alkylbenzene sulfonates with various points of attachment to the benzene ring. A comparison of the results for sodium alkyl sulfonates with those for alkylbenzene sulfonates (Tables 6.10 and 6.11) reflects the more hydrophilic nature of the aromatic ring as well as some branching-related effects. Analysis of the data indicates that, in terms of micellization effects, the benzene ring is approximately equivalent to 3.5 carbon atoms.

Surfactants that contain two hydrophobic chains, such as the sodium dialkyl sulfosuccinates, exhibit a number of interesting and useful properties that make it advantageous to understand their structure–property relationships. The work done on such materials has been limited by the

Table 6.9 The effect of sulfate substitution on the Klevens relationship (Eq. (6.17)) for C₂₀ alkyl sulfate surfactants at 40 °C.

Sulfate position	A	B
1	0.294	4.49
2	0.286	4.53
3	0.280	4.55
4	0.266	4.47
5	0.258	4.44
6	0.270	4.72
7	0.256	4.59
8	0.251	4.58
9	0.245	4.55
10	0.240	4.52

Table 6.10 The cmc's of some simple sodium alkyl sulfonate surfactants.

Surfactant	Temperature (°C)	cmc (mM)
C ₈ H ₁₇ SO ₃ [−]	40	160
C ₁₀ H ₂₁ SO ₃ [−]	40	41
C ₁₂ H ₂₅ SO ₃ [−]	40	9.7
C ₁₄ H ₂₉ SO ₃ [−]	40	2.5
C ₁₆ H ₃₃ SO ₃ [−]	50	0.7
C ₈ H ₁₇ OOC(CH ₂) ₂ SO ₃ [−]	30	46
C ₁₀ H ₂₁ OOC(CH ₂) ₂ SO ₃ [−]	30	11
C ₁₂ H ₂₅ OOC(CH ₂) ₂ SO ₃ [−]	30	2.2
C ₁₄ H ₂₉ OOC(CH ₂) ₂ SO ₃ [−]	40	0.9

Table 6.11 The cmc's of typical sodium alkylbenzene sulfonate surfactants.

Alkylbenzene group	Temperature (°C)	cmc (mM)
<i>p</i> -Hexyl	75	37
<i>p</i> -Heptyl	75	21
<i>p</i> -Octyl	60	15
<i>o</i> -Octyl	55	19
<i>p</i> -Nonyl	75	6.5
<i>p</i> -Decyl	50	3.8
<i>p</i> -Dodecyl	30	1.2
<i>p</i> -Tetradecyl	75	0.66
<i>p</i> -1-Methyldecyl	35	2.53
<i>p</i> -1-Methyldodecyl	35	0.72
<i>p</i> -1-Methyltetradecyl	40	0.31
<i>p</i> -1-Methylhexadecyl	50	0.13

general lack of isomeric purity of the commercial materials. The **cmc**'s of a few such materials, which were carefully purified, have been reported, however (Table 6.12). It can be seen that the **cmc** values for the straight-chain esters follow the Klevens relationship, although the value of **B** is slightly smaller than that found for single-chain surfactants. As might be expected, the **cmc**'s for the branched esters of equal carbon number occur at higher concentrations.

The addition of a benzene ring to the hydrophobic chain has an effect on the **cmc** similar to the addition of 3.5 $-\text{CH}_2-$ groups. Since many natural fatty acids serve as starting materials for synthetic surfactant manufacture, it is of interest to know what effect might be expected from the presence of ethylenic unsaturation in the chain. Some data for the **cmc**'s of saturated and unsaturated fatty acid analogues is given in Table 6.13. As can be seen, the presence of a single double bond in the chain increases the **cmc** by as much as a factor as 3–4 compared to the saturated compound. In addition to the electronic presence of the double bond, the isomeric configuration (*cis* or *trans*) will have an effect, with the *cis* isomer usually having a higher **cmc**, presumably because of the more difficult packing requirements imposed by the isomer.

If polar atoms such as oxygen or nitrogen are added to the hydrophobic chain (but not associated with a head group), the usual result is an increase in the **cmc**. The substitution of an $-\text{OH}$ for hydrogen, for example, reduces the effect of the carbon atoms between the substitution and the head group to half that expected in the absence of substitution. If the polar group and the head

Table 6.12 The **cmc**'s of typical surfactants containing two hydrophobic groups (not branched).

Surfactant	cmc (mM)
Sodium di- <i>n</i> -butylsulfosuccinate	200
Sodium di- <i>i</i> -butylsulfosuccinate	200
Sodium dipentylsulfosuccinate	53
Sodium dihexylsulfosuccinate	12.4
Sodium dioctylsulfosuccinate	6.8
$(\text{C}_8\text{H}_{17})_2(\text{CH}_3)_2\text{N}^+\text{Cl}^-$	26.6
$(\text{C}_{10}\text{H}_{21})_2(\text{CH}_3)_2\text{N}^+\text{Cl}^-$	2.0
$(\text{C}_{12}\text{H}_{25})_2(\text{CH}_3)_2\text{N}^+\text{Cl}^-$	0.18

Table 6.13 The effects of ethylenic unsaturation and polar substitution on the **cmc** of potassium soaps.

Carboxylate salt	Temperature (°C)	cmc (mM)
Octadecanoate (stearate)	60	0.5
Octadecenoate (oleate)	25	1.5
<i>trans</i> -9-Octadecenoate (elaidate)	50	1.5
$\text{C}_{19}\text{H}_{39}\text{COO}$ (abietate)	25	12
9,10-Dihydroxystearate	60	7.5
Ricinoleate	55	3.6

group are attached at the same carbon, that carbon atom appears to make no contribution to the hydrophobic character of the chain.

A number of commercial surfactants are available in which all or most of the hydrophobic character is derived from the presence of polyoxypropylene (POP) groups. The observed effect of such substitution on aggregation has been that each propylene oxide group is equivalent to approximately 0.4 $-\text{CH}_2-$ groups.

As demands placed on surfactants grow more stringent, new classes of materials have been developed that do not conveniently fit into the classical groupings of conventional hydrocarbon-based materials. These newer classes include those in which fluorine replaces hydrogen atoms on the carbon chain, silicone-based surfactants, and more recently “natural” surfactants and biosurfactants that can be a witch’s brew of protein, carbohydrate, and/or hydrocarbon units.

The hydrophobic unit of the silicone-based surfactants consists of low molecular weight polyorganosiloxane derivatives, usually polydimethylsiloxanes. Possibly because of their somewhat ill-defined structure and composition, they have received relatively little attention in the general scientific literature, although their unique surface characteristics have proved them useful in many technological applications, especially in nonaqueous systems.

Probably the most rapidly developing of the non-hydrocarbon surfactant families are the fluorocarbons. The substitution of fluorine for hydrogen on the hydrophobic chain has produced surfactants of several types with extremely interesting and useful properties. The presence of the fluorine atoms results in large decreases in critical micelle concentration relative to the corresponding hydrocarbon. The addition of one $-\text{CF}_2-$ group to a chain produces a much greater effect on the **cmc** than that of the $-\text{CH}_2-$ group. From the point of view of the general character of fluorinated materials, that observation is totally consistent with the lower cohesive energy density of fluorocarbon materials. One can say that fluorine atoms, once bound to carbon, are extremely happy and are reluctant to have extensive interactions with their neighbors.

Because of the electronic character of the carbon–fluorine bond, fluorinated materials have been found to exhibit much lower surface energies and surface tensions than conventional materials. The ability of polytetrafluoroethylene (PTFE or Teflon) to act as a nonstick coating, for example, results from the fact that the atoms in such a material do not interact strongly with those in adjoining phases, or themselves, for that matter. At the molecular level, the dispersion interactions among molecules are too weak to provide sufficient attraction for significant adhesion or cohesion to occur. That weakness of lateral molecular interactions is also reflected in the fact that fluorinated materials have boiling points much lower than would be expected based upon molecular weight considerations and that uncross-linked PTFE has very low mechanical strength. It has been the introduction of chemical cross-links into the technology that has brought us to the current state of the art in fluorocarbon coatings.

Fluorocarbons, hydrocarbons, and silicones exhibit widely differing cohesive energies as a result of the different natures of the $\text{C}-\text{C}-\text{F}$, $\text{Si}-\text{C}-\text{H}$, and $\text{C}-\text{C}-\text{H}$ bonds. Those differences reflect differences in the electronegativities of the various bond types. Surface energies and surface tensions can be related to those cohesive energy parameters. Liquids having the same number of carbon atoms show decreasing surface tensions in the order hydrocarbons > silicones > fluorocarbons.

A per-fluorinated surfactants will have all carbon–hydrogen bonds replaced by carbon–fluorine, so the simplest formula for the saturated materials will be $\text{CF}_3(\text{C}_n\text{F}_{2n})\text{S}$, where S signifies any of the possible surfactant head groups. Since various degrees of branching along the fluorocarbon chain are common, especially in commercial samples, care must be taken in the evaluation of such materials and the interpretation of experimental results. If hydrogen is substituted for a terminal

Table 6.14 Effect of hydrogen substitution on the **cmc**'s of fluorinated surfactants.

Surfactant	cmc (mM)
$\text{H}(\text{CF}_2)_6\text{COO}^- \text{NH}_4^+$	250
$\text{H}(\text{CF}_2)_8\text{COO}^- \text{NH}_4^+$	38
$\text{H}(\text{CF}_2)_{10}\text{COO}^- \text{NH}_4^+$	9
$\text{H}(\text{CF}_2)_6\text{COOH}$	150
$\text{H}(\text{CF}_2)_8\text{COOH}$	30
$\text{C}_5\text{F}_{11}\text{COOH}$	51
$\text{C}_7\text{F}_{15}\text{COOH}$	9
$\text{C}_9\text{F}_{19}\text{COOH}$	0.8
$\text{C}_5\text{F}_{11}\text{COO}^- \text{K}^+$	500
$\text{C}_7\text{F}_{15}\text{COO}^- \text{K}^+$	27
$\text{C}_7\text{F}_{15}\text{COO}^- \text{K}^+$	0.9

fluorine, there will be an increase in the **cmc** and the minimum surface tension the surfactant can produce in aqueous solution (Table 6.14).

When substitution occurs internally, leaving the terminal CF_3 intact, the effects are much less significant. This agrees with general observations that indicate that the surface energies of polymers and adsorbed monolayers are determined primarily by the top atomic layers, being less dependent on the chemical nature of succeeding layers. The fact that all CF_3 -terminated commercial surfactants do not produce the same low surface tension reflects molecular packing defects introduced by fluorocarbon chain branching, the presence of homologues and other impurities, and the steric demands of the various linking groups and head groups employed. In essentially all cases, however, the fluorinated materials will be significantly more surface active than the analogous hydrocarbon.

6.5.4 The Hydrophilic Group

As seen from the preceding section, the nature of the hydrophobic group has a major effect on the critical micelle concentration of a surfactant. The effect of the hydrophilic head group on the **cmc**'s of a series of surfactants with the same hydrocarbon chain may also vary considerably, depending on the nature of the change. In aqueous solution, for example, the difference in **cmc** for a C_{12} hydrocarbon with an ionic head group will lie in the range of 0.001 M, while a nonionic material with the same hydrocarbon chain will have a **cmc** in the range of 0.0001 M.

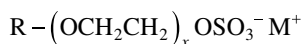
The **cmc**'s of several "model" surfactants are given in Table 6.15. It is evident from the data that the nature of the ionic head group has a rather small effect compared with that seen for changes in the hydrocarbon chain. Such a result is not surprising in view of the fact that the primary driving force in favor of micelle formation is the energy gain due to reduction of water-hydrophobe interactions, while the effect of the ionic group, beyond its impact on water solubility, is to work against the aggregation process. For all 1 : 1 electrolyte/paraffin chain salts that are completely dissociated, the electrical contribution to dissolution and to micelle formation will be relatively constant. Of course, differences in ionic radius, degree of hydration, and other non-electrical contributions will result in small differences among the various groups.

Table 6.15 The effect of the hydrophilic group on the **cmc**'s of surfactants with common hydrophobes.

Hydrophobe	Hydrophile	Temperature (°C)	cmc (mM)
C ₁₂ H ₂₅	COO ⁻ K ⁺	25	12.5
	SO ₃ ⁻ K ⁺	25	9.0
	SO ₃ ⁻ Na ⁺	25	8.1
	H ₃ N ⁺ Cl ⁻	30	14
	(CH ₃) ₃ N ⁺ Cl ⁻	30	20
	(CH ₃) ₃ N ⁺ Br ⁻	25	16
C ₁₆ H ₂₃	H ₃ N ⁺ Cl ⁻	55	0.85
	(CH ₃) ₃ N ⁺ Cl ⁻	30	1.3
	(CH ₃) ₃ N ⁺ Br ⁻	60	1.0
	(CH ₃) ₂ C ₂ H ₄ OH N ⁺ Cl ⁻	30	1.2
	(CH ₃)(C ₂ H ₄ OH) ₂ N ⁺ Cl ⁻	30	1.0
	(C ₂ H ₄ OH) ₃ N ⁺ Cl ⁻	30	1.0
C ₈ H ₁₇	OCH ₂ CH ₂ OH	25	4.9
	(OCH ₂ CH ₂) ₂ OH	25	5.8
C ₉ H ₁₉	COO(CH ₂ CH ₂ O) ₉ CH ₃	27	1.0
	COO(CH ₂ CH ₂ O) ₁₆ CH ₃	27	1.8
C ₁₀ H ₂₁	O(CH ₂ CH ₂ O) ₈ CH ₃	30	0.6
	O(CH ₂ CH ₂ O) ₁₁ CH ₃	30	0.95
	O(CH ₂ CH ₂ O) ₁₂ CH ₃	30	1.1

As noted earlier, the location of the head group along the hydrophobic chain can greatly affect micellization. It has been shown, for example, that as the charge on the hydrophilic group is moved away from the α -carbon of the hydrophobe, the **cmc** will decrease. Such a result has been attributed to the increased work required to move the charge toward a medium or low dielectric constant (the micellar core). Of the more common ionic head groups, the order of decreasing **cmc** values for a given hydrocarbon chain is found to be carboxylates (containing one more carbon atom) > sulfonates > sulfates.

The sulfated alkyl- and alkylbenzene polyoxyethylene chain is a class of ionic surfactants that has become increasingly important from an applications point of view. The basic structure of the family is



where x is the number of OE groups in the chain. These materials have found extensive use in many applications and are second only to the alkylbenzene sulfonates in total consumption worldwide. From the viewpoint of the physical chemistry of surfactants, it might be expected that the addition of oxyethylene groups adjacent to the ionic sulfate would increase the hydrophilic character of the molecule and modify the solution properties of the materials accordingly. In fact, when the terminal hydroxyl group of such nonionics is sulfated, a number of changes in solution characteristics do occur, but not necessarily those that might be expected from analogy with the related

Table 6.16 The effect of oxyethylene (OE) introduction between the hydrocarbon chain and sulfate group in $C_{12}H_{25}(OCH_2CH_2)_xOSO_3^- Na^+$ surfactants at 25 °C.

Number of EO(x)	cmc (mM)
0	8.0
1	0.5
2	0.3
4	0.2

nonionic structures. The critical micelle concentrations of a series of dodecyl oxyethylene sulfates with x varied from 1 to 4 are given in Table 6.16.

It can be seen that, contrary to what might be expected, the **cmc**'s of the materials decrease as each OE group is added, indicating an increase in the overall hydrophobicity of the molecules. Early speculation concerning such results focused on some effect that reduced the ionic character of the sulfate group in the presence of the oxyethylene linkages. Investigations into the degree of dissociation of alkyl ether sulfate micelles have shown, however, that in fact dissociation increases with x , the opposite to what would be expected for a decrease in **cmc**.

Additional anomalies can be found in the effect of added electrolyte on the **cmc**'s of these materials. It is usually found that the addition of electrolyte to solutions of ionic surfactants results in a decrease in the **cmc**, while nonionic materials are only slightly affected (see below). In the presence of 0.1N NaCl, the materials in Table 6.16 show a shift in **cmc** even greater than that found for the analogous dodecyl sulfate salt. It seems clear, then, that the combined effects of oxyethylene groups and ionic sulfates cannot be analyzed by simple analogy to either simple class of surfactants. In the absence of a clear-cut explanation for the unusual micellization properties of these materials, it has been suggested that the results might stem from either a reduction of the degree of hydration of the OE groups due to the presence of the sulfate or to a decrease in the work required to bring the ionic groups into close proximity during micelle formation as a result of the greater space requirements of the combination of hydrophiles. Data on the adsorption of alkyl ether sulfates onto solid surfaces and at the liquid/vapor interface, and data on micellar aggregation numbers, tend to support the importance of head group size and sulfate spacing to the micellization of these materials, especially for $x > 2$.

6.5.5 Counterion Effects on Micellization

As indicated by Eq. (6.12), the free energy of micelle formation for ionic surfactants contains a term related to the interactions of solvent, in most cases water, with the ionic head group. The degree of ionization of the ionic group, in terms of tight ion binding, solvent-separated ion pairing, or complete ionization, might be expected to greatly influence the magnitude of ΔG_m^w and consequently the **cmc** and aggregation number of the system. Since electrostatic repulsions among the ionic groups would be greatest for complete ionization, it is not surprising to find that the **cmc** of surfactants in aqueous solution decreases as the degree of ion binding increases.

From regular solution theory it is found that the extent of ion pairing in a system will increase as the polarizability and valence of the counterion increase. Conversely, a larger radius of hydration will result in greater ion separation. It has been found that, for a given hydrophobic tail and anionic

Table 6.17 The **cmc**'s of various metal salts of dodecyl sulfate.

Counterion	Temperature (°C)	cmc (mM)
Li ⁺	25	8.8
"	40	10.5
Na ⁺	25	8.1
"	40	8.9
K ⁺	40	7.8
Cs ⁺	40	6.9
(CH ₃) ₄ N ⁺	25	5.6
(1/2 Ca ²⁺)	54	2.6
(1/2 Mg ²⁺)	25	1.6
(1/2 Zn ²⁺)	60	2.1

head group, the **cmc** generally decreases in the order Li⁺ > Na⁺ > K⁺ > Cs⁺ > N(CH₃)₄⁺ > N(CH₂CH₃)₄⁺ > Ca²⁺ ≈ Mg²⁺. In the case of cationic surfactants such as dodecyl trimethylammonium halides, the **cmc**'s are found to decrease in the order F⁻ > Cl⁻ > Br⁻ > I⁻.

Although within a given valency the size of the hydrated counterion will have some effect on the micellization of an ionic surfactant, a more significant effect is produced by changes in valency. As the counterion is changed from monovalent to di- and trivalent, the **cmc** is found to decrease rapidly. The **cmc**'s of various salts of dodecyl sulfate are listed in Table 6.17. As discussed earlier, the divalent and higher salts of carboxylic acid soaps generally have very low water solubility and are not useful as surfactants in aqueous solution. They have found use in nonaqueous solvents because of their increased solubility in those systems, especially in the preparation of water-in-oil emulsions. As we will see, the presence of ions in aqueous surfactant solutions beyond the stoichiometric concentration can produce a more significant effect than changes within a valency group.

6.5.6 The Effects of Additives on the Micellization Process

Most industrial applications of surfactants involve the presence in the solution of co-solutes and other additives that can potentially affect the micellization process through specific interactions with the surfactant molecules (thereby altering the effective activity of the surfactant in solution) or by altering the thermodynamics of the micellization process by changing the nature of the solvent or the various interactions, leading to or opposing micelle formation. Examples of specific interactions between surfactant molecules and co-solutes are common when the system contains polymeric materials. Because of the growing importance of such systems, they are treated as a special topic in Chapter 8.

In the absence of specific interactions, which can be quite complex, it is useful to be able to rely on laboratory **cmc** and aggregation number data to predict the characteristics of micellization of a surfactant in use. The use of such data, however, must be tempered by the knowledge that it is only really valid if the conditions of use parallel those under which the measurements are made. The reality of surfactant life is that in many applications, such parallelism may not, in fact, apply.

The solution changes commonly encountered in use that might be expected to impact the process include (i) the presence of electrolyte, (ii) changes in pH, (iii) the presence of organic materials

that may be essentially water insoluble (e.g. hydrocarbons), (iv) the presence of water miscible co-solvents, (v) the presence of materials that have low water solubility but that contain polar groups that impart some surface activity although they are not classified formally as surfactants, and (vi) the presence of polymeric materials. In the brief discussion of each category that follows, it must be remembered that each surfactant system can exhibit characteristics different from the general observations noted here.

6.5.6.1 Electrolyte Effects on Micelle Formation

In aqueous solution, the presence of electrolytes causes a decrease in the **cmc** of most surfactants, with by far the greatest effect being found for ionic materials. For such materials, the effect of addition of electrolyte on the **cmc** can be empirically quantified with the relationship

$$\log_{10} \text{cmc} = -a \log_{10} c_i + b \quad (6.25)$$

where **a** and **b** are constants for a given ionic head group at a particular temperature and c_i is the total concentration of monovalent counterions in moles per liter.

The lowering of the **cmc** is primarily due to a reduction in the electrostatic repulsion between head groups and, consequently, a smaller contribution of those groups to the free energy term opposing micellization (ΔG_m^w , Eq. (6.20)). For nonionic and zwitterionic materials, the impact of added electrolyte is significantly less, and the relationship in Eq. (6.20) does not apply. For such surfactants, a relationship of the form

$$\log_{10} \text{cmc} = -K C_s + \text{constant} \quad (\text{for } C_s < 1) \quad (6.26)$$

has been suggested, where **K** is a constant for a particular surfactant, electrolyte, and temperature and C_s is the concentration of added electrolyte in moles per liter. For alkyl betaines it has been found that the value of **K** in Eq. (6.26) increases with an increase in the length of the hydrophobic chain and with the charge on the anion of the electrolyte.

The observed changes in the **cmc** of nonionic and zwitterionic materials with the addition of electrolytes cannot be attributed to the same electrostatic effects as for fully ionic surfactants. The most generally accepted explanation of such effects has been developed in the context of changes in the solvent properties of the aqueous solution for the hydrophobic group and the degree of solvation of the hydrophilic. It is well known that the solubility of many materials in water can be significantly altered by the addition of neutral ions. The result of such addition can be a reduced solubility, commonly referred to as “salting out” or increased solubility or “salting in.” The specific effect will depend upon the nature of the added electrolyte.

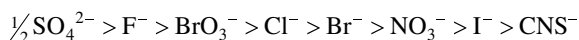
It has also been suggested that the changes in **cmc** found for nonionic materials with electrolyte addition are related to the amount of work required to disrupt the structure of the aqueous solvent by the insertion of the surfactant molecule. If added electrolyte acts to enhance structure, that is, if it increases the organization of the water molecules through the action of the added ions, the introduction of the monomeric surfactant molecule will require an additional amount of work to overcome that added structural energy. The net result will be a “salting out” of the surfactant and a decrease in the **cmc**. If, on the other hand, the added electrolyte acts as a structure breaker, the required work will be less, the surfactant will be “salted in,” and the **cmc** will increase.

Nonionic surfactants that have highly hydrogen bonding interactions in water such as POE ethers and sugar esters will often not show significant salt effects until the electrolyte concentration reaches the level at which the activity of the water becomes affected. At that point, the

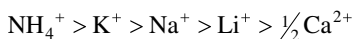
competition between the dissolved salts and the hydrophilic group for the available water becomes intense, and the **cmc** will be found to decrease. The same might be expected for the addition of nonionized additives that have a similar interaction with water such as sugars and other polyhydroxy materials, organic acids and amines, water soluble polymers, etc.

In the case of the POE nonionic surfactants, there exists an additional possible phenomenon that may help to explain the effect of certain cations on their properties. It is well known, for example, that the cyclic polyoxyethylene or “crown” ethers can form very strong complexes with many appropriately sized ions such as Na^+ and K^+ . When the ionic radius of the ion is properly matched to the size of the “basket” formed by the cyclic ether, interactions between the ether oxygen atoms and the ion produce complexes with exceedingly large stability constants. It seems reasonable to expect that linear POE chains of intermediate length, relatively free to assume various configurations in solution, could do so in such a way as to form a “pseudo-crown” ether capable of forming complexes with cationic ions. Should such a phenomenon occur, either with the monomer or the micelle, we would expect the overall thermodynamics of the system to be affected, including that of the micellization process. Such a scenario is presently somewhat speculative, but it represents an interesting potential field for further research.

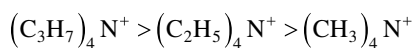
The effectiveness of a given ion at altering the micellization process can be qualitatively related to the radius of hydration of the added ions, with the contribution of the cations and anions being approximately additive. In general, the smaller the radius of hydration of the ion, the greater is its effect on the **cmc**. The approximate order of effectiveness of anions at decreasing the **cmc** is the following:



For cations, the order is



It has been found that the tetraalkylammonium salts of surfactants exhibit an increase in the **cmc** in the order



6.5.6.2 The Effect of pH

Since most modern, industrially important surfactants consist of long-chain alkyl salts of strong acids, it might be expected that solution pH would have a relatively small effect, if any, on the **cmc** of the materials, an expectation generally borne out by experience. In solutions of sulfonate and sulfate salts, where the concentration of acid or base significantly exceeds that of the surfactant, the excess will act as if it were simply neutral electrolyte with roughly the same results as discussed above.

Unlike the salts of strong acids, the carboxylate soap surfactants exhibit a significant sensitivity to pH. Since the carboxylate group is not fully ionized near or below the pK_a , the electrostatic interactions between head groups retarding micelle formation will vary with the solution pH, resulting in significant changes in the **cmc**. A similar result will be observed for the cationic alkylammonium salts near and above the pK_b , resulting in a decrease in the **cmc**. When the surfactant is in the fully ionized form, excess acid or base will act as neutral electrolyte as mentioned above.

It is to be expected that pH will have no effect on the **cmc** of nonionic surfactants, and that is generally found to be the case. However, at very low pH it is possible that protonation of the ether oxygen of OE surfactants could occur. Such an event would, no doubt, alter the characteristics of the system. Little can be found in the literature pertaining to such effects, however.

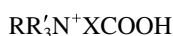
A number of amphoteric surfactant systems show pH sensitivity related to the **pK**'s of their substituent groups. At low pH, materials containing carboxyl and amine groups would act as cationic surfactants, while at high pH the activity would be anionic by analogy to the action of amino acids. If the cation is a quaternary ammonium salt, no pH sensitivity would be expected, as would be the case for a strong acid anionic group. The pH sensitivity of amphoteric surfactants, therefore, will vary according to the specific structure of the materials. The possibilities can be grouped in the following way:

- 1) Quaternary ammonium/strong acid salt with no significant pH sensitivity



where R is a long-chain alkyl group, R' is a short-chain alkyl, and X is a linking carbon chain usually of one or two carbons.

- 2) Quaternary ammonium/weak acid, which will be zwitterionic at high pH and cationic below the **pK_a** of the acid



where R, R', and X are as defined in item 1.

- 3) Amine/weak acid, which will be anionic at high pH, cationic at low pH, and zwitterionic at some pH between the respective **pK**'s of the groups



where at least one of R' or R'' is a hydrogen.

- 4) Amine/strong acid, which will be anionic at high pH and zwitterionic below the **pK_b** of the amine



6.5.6.3 The Effects of Added Organic Materials

Organic materials that have low water solubility can be solubilized in micelles to produce systems with substantial organic content where no solubility would occur in the absence of surfactant. The details of the phenomenon of solubilization in surfactant micelles are presented in Chapter 8. Here we are concerned only with the possible effects of the phenomenon on the micellization process itself.

In the process of solubilization of water-immiscible organics in micelles, the size of the aggregate, and therefore the curvature of its surface, can change significantly. In the presence of such changes, it can be expected that there will be changes in the energetic requirements of interactions among the component parts of the surfactants in the micelle, especially the head groups at the micelle surface. Changes in the hydrophobic interactions among the hydrocarbon tails due to the insertion of additive molecules into the core may also occur. The combined effect of the presence of the solubilized material is usually to produce a slight decrease in the measured **cmc** of the

Table 6.18 The effect of organic additives on the **cmc**'s of ionic surfactants.

Surfactant	Additive (mM)	cmc (mM)
$C_{12}H_{25}NH_3^+ Cl^-$	Cyclohexane	(0) 1.45
	"	(1.54) 1.34
	"	(2.5) 1.30
	"	(4.2) 1.20
	Heptane	(0.87) 1.34
	"	(2.12) 1.31
	"	(2.72) 1.28
	Toluene	(0.78) 1.40
	"	(2.19) 1.35
	"	(2.96) 1.31
$C_{10}H_{21}SO_3^- Na^+$	Benzene	(0) 41
		(34) 38
$C_{12}H_{25}SO_3^- Na^+$	Benzene	(0) 9.7
		(7.5) 9.2
$C_{14}H_{29}SO_3^- Na^+$	Benzene	(0) 2.5

system. The effect, however, is usually substantially smaller than that observed for the addition of electrolyte or changes due to structural changes in the surfactant molecule.

The effects of added organic materials on the **cmc** of some ionic surfactants are shown in Table 6.18. From the results it is evident that the effects, while relatively small, can be experimentally significant, especially as the length of the hydrocarbon tail of the surfactant increases. Because of these effects, it becomes necessary to assess the results of **cmc** determinations using the dye solubilization technique with the thought in mind that the solubilization process could conceivably alter the **cmc** of the system.

Organic additives with substantial water miscibility such as the lower alcohols, dioxane, acetone, glycol, and tetrahydrofuran would not be expected to partition into the interior of the micelle when present in small amounts. The effect of such materials on the **cmc**, therefore, would be expected to be relatively minor. As the carbon number of the additive goes beyond C_2 , the inherent surface activity of the alcohol can start to become significant. Otherwise, it will be only at high concentrations, where the additive may be considered to be a co-solvent, that major effects on **cmc** will be evident. Those effects will be the result of changes in the bulk solvent properties of the system. The energy requirements for bringing the hydrophobic tail into solution may decrease, leading to an increase in the **cmc**. Conversely, the added organic material will result in a reduction in the dielectric constant of the solvent mixture. Such an effect would tend to decrease the **cmc** of ionic surfactants as a result of their lower solubility and reduced repulsion between adjacent head groups at the micellar surface. The net effect on the **cmc** will therefore depend on the relative magnitudes of the two opposing trends. In any case, the effects are usually found to be relatively minor until substantial additive concentrations are reached.

The properties of a surfactant solution are found to change much more rapidly with the introduction of small amounts of long-chain alcohols, especially C_4 and greater. Because so many classes of surfactants of importance academically and industrially are derived from alcohols or raw

Table 6.19 The effect of added alcohol chain length (as change in **cmc** with alcohol concentration, $\delta_{\text{cmc}}/\delta C_a$) on potassium carboxylate surfactant **cmc**'s.

Alcohol	$\delta_{\text{cmc}}/\delta C_a$			
	C ₇ COOK (10 °C)	C ₉ COOK (10 °C)	C ₁₁ COOK (10 °C)	C ₁₃ COOK (18 °C)
C ₃ OH	0.14	0.065	0.012	0.0032
C ₄ OH	0.38	0.19	0.038	0.0098
C ₆ OH	3.6	1.3	0.37	0.098
C ₈ OH	23	8.3	3.5	1.0
C ₁₀ OH	112	55	18	8.1

materials containing alcoholic impurities, the recognition of the effects of such materials can be very important. Most of the observed effects can be attributed to the inherent surface activity of the longer alcohols – preferential adsorption at interfaces and a high proclivity for mixed micelle formation.

A number of studies have been carried out to determine the relationships among such factors as the number of carbon atoms in the alcohol chain, that of the surfactant tail, the alcohol concentration, and the observed **cmc** of the system. A useful logarithmic relationship has the form

$$\ln \left[-(\delta_{\text{cmc}}/\delta C_a) \right] = -0.69m + 1.1m_a + \text{constant} \quad (6.27)$$

where **m** and **m_a** are the number of carbon atoms in the surfactant chain and the alcohol, respectively, and **C_a** is the molar concentration of alcohol in the mixture. The term $-(\delta_{\text{cmc}}/\delta C_a)$ is derived from a plot of **cmc** versus **C_a**. It is generally found that alcohols of carbon numbers 2–7 follow Eq. (6.27) rather well, while deviations begin to occur for the higher alcohols (Table 6.19), presumably because of the difficulty of packing the longer alcohol chains into the micellar structure.

The interactions between surfactants and alcohols have become of greater importance in recent years as a result of the intense interest in microemulsions and their potential application in various areas of technological importance. Because of the rapid rate and volume of publications in the area of microemulsion technology, often emphasizing surfactant-additive interactions, Chapter 7 includes a summary of some current thinking on the subject.

6.5.7 The Effect of Temperature on Micellization

The effects of temperature changes on the **cmc** of surfactants in aqueous solution have been found to be quite complex. It is found, for example, that the **cmc** of most ionic surfactants passes through a minimum as the temperature is varied from about 0° through 60–70 °C. Nonionic and zwitterionic materials are not quite so predictable, although it is found that some nonionic materials reach a **cmc** minimum around 50 °C.

When one considers the possible reasons for the observed temperature effects on **cmc**, it seems clear that one area of impact is in the degree of hydration of the head group, since the structuring of water molecules is known to be very temperature sensitive. As the temperature of the system is increased, the degree of water–solute hydration will decrease, as will the cohesive

interactions among water molecules. On one hand, the result will be a decrease in the energy factors favoring solution and an increase in the tendency toward micelle formation. On the other hand, the factors that reduce head group hydration at higher temperatures will also reduce energy increase caused by the structured water molecules around the hydrophobic portion of the surfactant molecule. The result from that scenario will be a reduction of the magnitude of the free energy component attributable to the hydrophobic or entropic effect (ΔG_m^h , Eq. (6.18)). Such an effect will increase the “solubility” – or more accurately, decrease the “insolubility” – of the tail in water, a result that is in opposition to micelle formation. Since the two temperature effects act in opposite directions, the net effect of increasing or decreasing the **cmc** will depend on the relative magnitudes of the two.

The temperature dependence of the **cmc**'s of polyoxyethylene nonionic surfactants is especially important, since the head group interaction is essentially totally hydrogen bonding in nature. Materials relying solely on hydrogen bonding for solubilization in aqueous solution are commonly found to exhibit an inverse temperature/solubility relationship. A major manifestation of such a relationship is the presence of the so-called cloud point for many nonionic surfactants.

The “cloud point,” as defined, is the temperature at which the solubility of the nonionic surfactant is not sufficient to provide the solubility necessary for effective surfactant action. In essence, it is a lower critical solution temperature for the low molecular weight POE chain. At the cloud point, a normally transparent solution of nonionic surfactant becomes cloudy, and bulk phase separation occurs. That is not to say that the material precipitates from solution; rather, a second swollen phase containing a high fraction of the POE surfactant appears, and its domains are significantly larger than those of a normal micelle.

Because of the role of the POE units in providing solubility to nonionic surfactants, it is not surprising to find that such surfactants with relatively short POE chains possess cloud points in easily accessible temperature ranges (Table 6.20). They usually do not pass through a minimum in the **cmc-T** curve. If one considers a surfactant with 10 OE units, the loss of one hydrogen bond represents a loss of 10% of the energy contributing to solution of the monomeric species. For a surfactant with 20 OEs, such a change will represent a loss of only 5%. Clearly, then, the situation of the nonionic surfactants is complicated by the possibility of phase separation occurring before the increased “solubility” of the hydrophobe can bring about a balancing increase in the **cmc**.

Table 6.20 Cloud points (1% soln.) of representative (average) POE nonionic surfactants.

Surfactant	Cloud point (°C)
$C_9H_{19}COO(CH_2CH_2O)_7CH_3$	44
$C_9H_{19}COO(CH_2CH_2O)_{10}CH_3$	65
$C_9H_{19}COO(CH_2CH_2O)_{12}CH_3$	74
$C_9H_{19}COO(CH_2CH_2O)_{16}CH_3$	>100
$C_{11}H_{23}COO(CH_2CH_2O)_6CH_3$	31
$C_{11}H_{23}COO(CH_2CH_2O)_8CH_3$	53
$C_{11}H_{23}COO(CH_2CH_2O)_{10}CH_3$	74
$C_{11}H_{23}COO(CH_2CH_2O)_{12}CH_3$	79

6.6 Micelle Formation in Mixed Surfactant Systems

When one discusses the solution behavior of many, if not most, industrial surfactants, it is important to remember that experimental results must be interpreted in the context of a surfactant mixture rather than a pure homogeneous material. Studies of such systems are important both academically, assuming that the mixture can be properly analyzed as to its composition, and practically, since most detergents and soaps contain homologues of higher or lower chain length than that of the primary or “average” component.

Determinations of the **cmc** of well-defined binary mixtures of surfactants have shown that the greater the difference in the **cmc** between the components of the mixture, the greater is the change in the **cmc** of the more hydrophilic member of the pair as the chain length of the more hydrophobic member is increased. Early analyses of the solution behavior of binary surfactant mixtures seemed to indicate that even homologous surfactants gave non-ideal mixing in solution. It has since been recognized, however, that the analysis of the results must take into consideration the fact that at the **cmc**, the mole fractions of the monomeric surfactants in solution are not equal to the stoichiometric mole fractions; each value must be decreased by the amounts of each mole fraction incorporated into the micellar phase.

Theories describing the phenomena relating to the **cmc** of surfactant mixtures and their respective compositions have been developed by considering the effective mole fraction of each species in a binary mixture at the **cmc**. Although there is generally good agreement between the theory and experiment, in cases in which there is a large enough difference between the chain lengths of the two surfactants, significant deviations have been found. The observed differences have been explained by such effects as (i) relatively small changes in the mole fraction of the smaller chain component due to preferential aggregation of the more hydrophobic material (i.e. homogeneous micelle formation) and (ii) the difficulty of inclusion of the longer chain into micelles of the shorter material. In some cases, where the difference is very large, the shorter component may well act as an added electrolyte, with the consequent effects to be expected from such an addition, rather than becoming directly involved in the micellization process. When ternary surfactant mixtures are considered, it is usually found that the **cmc** of the mixture will fall somewhere between that of the highest and lowest value determined for the individual components.

The critical micelle concentrations of mixtures of POE nonionic surfactants are of particular interest, since the synthesis of such materials on a commercial basis will always produce a rather broad range of POE chain lengths. Because they contain no electrostatic contribution to the free energy of micelle formation, they can be treated theoretically with a simpler relationship between composition and **cmc**. In a mixture of nonionic surfactants in which the average POE chain lengths are approximately the same and the hydrocarbon chains different, there was a smooth decrease in the **cmc** of the mixture as the mole fraction of the more hydrophobic material (lower **cmc**) was increased, reminiscent of the surface tension–mole fraction curves found for miscible organic materials mixed with water.

The critical micelle concentrations of mixtures of ionic and nonionic surfactants has not been as fully explored as that of mixtures of structurally related materials, although it appears as if such systems are reasonably well behaved. Using the assumption that the mole fraction of ionic and nonionic surfactants in the micelle is the same as the bulk ratio, a good correlation can be made between micellar aggregation number, **cmc**, and the composition of the mixture.

The presence of an ionic surfactant in mixture with a nonionic usually results in an increase in the cloud point of the nonionic component. In fact, the mixture may not show a cloud

point, or the transition may occur over a broader temperature range, indicating that the ionic component is forming mixed micelles with the nonionic surfactant, thereby increasing its “solubility” at higher temperatures. As a result, it is possible to formulate mixtures of ionic and nonionic surfactants for use at temperatures and under solvent conditions (electrolyte, water soluble organic materials, insoluble organic materials, etc.) in which neither component alone would be effective.

As will be seen in subsequent chapters, many mixtures of surfactants, especially ionic with non-ionic, exhibit surface properties significantly better than those obtained with either component alone. Such synergistic effects greatly improve many technological applications in areas such as emulsion formulations, emulsion polymerization, surface tension reduction, coating operations, personal care and cosmetic products, pharmaceuticals, and petroleum recovery, to name a few. The use of mixed surfactant systems should always be considered as a method for obtaining the optimal performance for any practical surfactant application.

A more unique and less extensively researched class of mixed surfactant systems is that in which the two components are of opposite charge, that is, a mixture of a cationic and an anionic surfactant. In aqueous solvents such mixtures will often result in precipitation of stoichiometric amounts of the two materials due to ion pairing of the two surface-active components. A very careful combination of the two ionic classes can produce interesting results in terms of surface tension lowering (effectiveness) due to the formation of close ion pairs in the surface monolayer. In non-aqueous solvents, on the other hand, interesting and useful results may be obtained since the ion-paired combination may be significantly soluble in the organic solvent while still retaining useful properties in terms of aggregation and adsorption. Some such combinations have shown promise as phase transfer catalysts in which one or both components act as “mules” to shuttle reactants and products between aqueous and organic phases.

As fluorinated surfactants become more widely used throughout industry, regulatory constraints permitting, there often arise needs for a mixture of hydrocarbon and fluorocarbon materials to meet system performance requirements. For example, fluorocarbon surfactants are excellent at lowering the surface tension of aqueous systems at very low concentrations but are normally of little use for forming or stabilizing emulsions. In systems requiring a low surface tension and emulsion stabilization, it may be convenient to use both classes of materials. In such instances it must be determined whether the two types of surfactant will form mixed micelles or whether two different types of homogeneous micelles will result. The presence of two distinct micellar types in a single solution, with all the accompanying characteristic differences, poses many interesting theoretical and practical questions. One might expect that given the known immiscibility of heavily fluorinated materials with hydrocarbons, co-micellization would not be the rule. Although the experimental data are limited, there seems to be good evidence that the formation of two micellar species does occur in many instances.

6.7 Micelle Formation in Nonaqueous Media

The formation of surfactant aggregates in nonaqueous solvents has received far less attention than the related phenomenon in water. In the present context, the term “nonaqueous” refers primarily to organic solvents such as hydrocarbons, aromatics, halogenated materials, and other liquids of low polarity and low dielectric constant. It does not generally include, for example, such solvents as dimethylformamide (DMF), dimethylsulfoxide (DMSO), the lower alcohols ($C < 4$), etc., although they will be briefly mentioned below.

In the past there was some controversy as to whether such a phenomenon as surfactant aggregation in fact occurs in the same sense as in aqueous solutions. There is no doubt that some chemical species, many surfactants included, do undergo an aggregation process in hydrocarbon and other nonpolar solvents. It is well known, for example, that carboxylic acids will dimerize in benzene, as evidenced by the fact that the molecular weights determined by boiling point elevation are routinely twice that of the monomeric species. Overwhelming experimental evidence, however, points to the fact that many other chemical types not only dimerize but also form relatively large aggregates in nonpolar solvents that must be considered to be related to, if not identical to, the micelles formed in aqueous systems. Whether one prefers to call such species micelles, reversed micelles, or inverted micelles or to use some other terminology, the characteristics and applications of those species warrant their inclusion in the current discussion.

6.7.1 Aggregation in Polar Organic Solvents

In polar solvents such as glycerol, ethylene glycol, dimethylsulfoxide, and formamide, many nonionic surfactants such as the POE alkylphenols aggregate to form micelles resembling those in aqueous solution. No micelles appear to be formed, however, in solutions of the lower alcohols or related solvents. Some attempts have been made to correlate the logarithms of the **cmc**'s of such nonionic surfactants with the solubility parameters of the solvents employed. In several polar solvents, the free energy of micellization of $C_{12}H_{25}-(OE)_n$ surfactants with $n = 4, 6$, and 8 has been resolved into the hydrocarbon and polar group contributions. In all the systems studied, the nature of the hydrocarbon chain has been identified as the most important factor driving the system toward micellization.

Many surfactant applications, especially those related to pharmaceuticals, require the presence of mixed solvent systems. The nonionic $C_{12}H_{25}-(OE)_6$ was found to form micelles in solutions of water, formamide, and mixtures of the two. Increasing the amount of formamide in the mixture led to an increase in the **cmc**. In aqueous solutions of sodium dodecylsulfate, the **cmc** is initially decreased by the addition of ethyl alcohol, reaches a minimum at about 5% alcohol, and increases from that point. The initial decrease in **cmc** is attributed to the preferential association of the ethanol with the surfactant micelle, followed by an increase in the solubility of the surfactant monomer as the solvent became less aqueous in character. Similar behavior has been observed for aqueous solutions containing nonionic surfactants and other water-miscible organic solvents.

The forces leading to micelle formation in polar organic solvents are not well understood, but they probably lie somewhere between the classical aqueous driving forces and the more or less opposite phenomena operating in nonpolar systems. There is undoubtedly a spectrum of mechanisms to be explored on theoretical and practical grounds for the ambitious graduate student or industry intern.

6.7.2 Micelles in Nonpolar Solvents

One of the reasons for the scarcity of information on nonaqueous micelles is the relative difficulty of obtaining good, reproducible data. In water, micellization can be relatively easily followed using laboratory techniques such as surface tension measurements, conductivity, light scattering, dye solubilization, etc. In organic media, the two classic workhorses of surfactant studies, surface tension and conductivity measurements, are pretty useless. Dye solubilization has been used but tends to be difficult to repeat quantitatively. A number of spectroscopic techniques have also been used with varying degrees of success. However, because the aggregation process in organic solvents

is apparently not a sudden onset phenomenon like in water, the identification of the exact concentration of surfactant present when the process occurs is often subject to a wide range of interpretations. Precise data, therefore, is hard to come by.

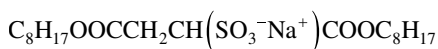
The forces and changes involved in surfactant aggregation in nonpolar nonaqueous solvents differ considerably from those already discussed for water-based systems. The orientation of the surfactant relative to the bulk solvent will be the opposite to that in water (hence the term “reversed” micelle, Figure 6.5c). In addition, the micelle, regardless of the nature of the surfactant, will be unionized in solvents of low dielectric constant and thus will have no significant electrical properties relative to the bulk solvent. Electrostatic interactions may, as we shall see, play an important role in the aggregation process but in an opposite sense to that in aqueous solution where strong head group repulsion tended to work against micelle formation.

As pointed out previously, the primary driving force for the formation of micelles in aqueous solution is the unfavorable entropic effect – also referred to as the “hydrophobic effect” in some literature – of ordering water molecules around the surfactant tail. In nonaqueous solvents, that effect would not be expected to be important since there would be little energy difference between solvent–solvent, solvent–tail, and tail–tail interactions. That is the case even if the solvent is aromatic or halogenated, rather than a simple hydrocarbon. Systems containing fluorinated materials or silicones are possible exceptions, as indicated by the fact that the surface tensions of some organic liquids are lowered by such surfactants. A more significant energetic consequence of nonaqueous micelle formation is the reduction of unfavorable interactions between the polar or ionic head groups of the surfactant molecules and the nonpolar solvent molecules. By analogy, such an effect might be called a “hydrophilic effect.”

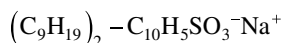
Unlike the situation for aqueous micelles, in which interactions among the hydrophobic tails contribute little to the overall free energy of micelle formation, ionic, dipolar, or hydrogen bonding interactions between head groups in reversed micelles may be the primary driving forces driving micelle formation. In the face of factors favoring aggregation, there seem to be few obvious factors opposing the formation of nonaqueous micelles, such as head group repulsion. The possible exception is unfavorable entropy losses as a result of fewer degrees of freedom for monomers in the micelle relative to those free in solution.

Of the many possible reasons for the relative scarcity of experimental data on nonaqueous micelles versus the aqueous variety, one of the most important is the failure of the easy and straightforward techniques applicable in water to work in most nonaqueous situations. Particularly important are the measurements of conductivity and surface tension. The ionization of charge-carrying species in solvents of low dielectric constant is, of course, difficult at best, and very high potentials are required to make electrochemical measurements in such systems. In addition, since most surfactants possess hydrocarbon tails, their adsorption at the solution–air interface, if it occurs, will be such that the polar head group is directed outward, a situation that could actually result in an increase in measured surface tension. Materials that can produce a lowering of the surface tension of organic solvents, namely, fluorocarbons and silicones, usually do so in a smooth decrease over a few millinewton per meter, so a phenomenon such as a **cmc** cannot be readily defined.

Unlike aqueous surfactant solutions in which micellar size and shape may vary considerably, small spherical micelles appear to be the most favored, especially when the reduction of solvent/polar group interactions is important. Similar to water-based systems, geometric considerations often play an important role in determining micelle size and shape. Many materials that commonly form nonaqueous micellar solutions possess large, bulky hydrocarbon tails with a cross-sectional area significantly greater than that of the polar head group. Typical examples of such materials are sodium di-2-ethylhexylsulfosuccinate and sodium dinonylnaphthalene sulfonate:



and



Since unambiguous experimental data are much less available on micelle formation in nonaqueous solvents, it is far more difficult to identify trends and draw conclusions concerning the relationships between chemical structures and critical micelle concentrations and aggregation numbers. Some compilations of such data are given in Tables 6.21 and 6.22. Because of the difficulties of obtaining precise data and the limited number of systems available, the numbers cited should be taken as approximate values that can change significantly if the conditions vary. For example, in hydrocarbon solvents, the nature of the polar head group is extremely important in the aggregation process. It has generally been found that ionic surfactants form larger nonaqueous micelles than nonionic ones, with anionic sulfates surpassing the cationic ammonium salts. The aggregation number for dinonylnaphthalene sulfonate in benzene was found to be essentially constant for a series of 10 different counterions, indicating a lack of sensitivity to the nature of the cation.

Table 6.21 Critical micelle concentrations for some surfactants in organic media.

Surfactant	Temperature (°C)	Solvent	cmc (mM)
Na^+ Di-2-ethylhexylsulfosuccinate	30	Cyclohexane	1.6
Na^+ Di-2-ethylhexylsulfosuccinate	30	Benzene	3
Na^+ Di-2-ethylhexylsulfosuccinate	30	Dodecane	3
Li^+ Dinonylnaphthalenesulfonate	25	Cyclohexane	1.1
Na^+ Dinonylnaphthalenesulfonate	25	Benzene	0.1–1
Ba^{2+} Dinonylnaphthalenesulfonate	25	Benzene	0.1–1
$n\text{-C}_{12}\text{H}_{25}\text{NH}_3^+ \text{C}_2\text{H}_5\text{COO}^-$	25	Benzene	2.2
$n\text{-C}_{12}\text{H}_{25}\text{NH}_3^+ \text{C}_3\text{H}_7\text{COO}^-$	25	Benzene	1.8
$n\text{-C}_{12}\text{H}_{25}\text{NH}_3^+ \text{C}_4\text{H}_9\text{COO}^-$	25	Benzene	2.0
$n\text{-C}_{12}\text{H}_{25}\text{NH}_3^+ \text{C}_3\text{H}_7\text{COO}^-$	25	Cyclohexane	2
$n\text{-C}_{12}\text{H}_{25}\text{NH}_3^+ \text{C}_3\text{H}_7\text{COO}^-$	25	CCl_4	1.6
$n\text{-C}_{18}\text{H}_{37}\text{NH}_3^+ \text{C}_2\text{H}_5\text{COO}^-$	25	Benzene	8
$n\text{-C}_{18}\text{H}_{37}\text{NH}_3^+ \text{C}_3\text{H}_7\text{COO}^-$	25	Benzene	2.7
$n\text{-C}_{12}\text{H}_{25}(\text{OCH}_2\text{CH}_2)_4\text{OH}$	—	Benzene	1.6
$n\text{-C}_{13}\text{H}_{27}\text{O}(\text{CH}_2\text{CH}_2)_6\text{OH}$	—	Benzene	2.6
$n\text{-C}_{12}\text{H}_{25}(\text{OCH}_2\text{CH}_2)_4\text{OH}$	—	Benzene	1.6
$n\text{-C}_{13}\text{H}_{27}\text{O}(\text{CH}_2\text{CH}_2)_6\text{OH}$	—	Benzene	2.6
$(n\text{-C}_7\text{COO}^-)_2 \text{Zn}^{2+}$	—	Toluene	6
$(n\text{-C}_9\text{COO}^-)_2 \text{Zn}^{2+}$	—	Toluene	5
$(n\text{-C}_{11}\text{COO}^-)_2 \text{Zn}^{2+}$	—	Toluene	4

Table 6.22 The aggregation number for several surfactants in nonaqueous solvents.

Surfactant	Temperature (°C)	Solvent	Aggregation number
<i>n</i> -C ₉ COOCH ₂ CHOHCH ₂ OH	30	Benzene	41
<i>n</i> -C ₉ COOCH ₂ CHOHCH ₂ OH	30	Cl-benzene	16
<i>n</i> -C ₁₁ COOCH ₂ CHOHCH ₂ OH	30	Benzene	73
<i>n</i> -C ₁₁ COOCH ₂ CHOHCH ₂ OH	30	Cl-benzene	47
<i>n</i> -C ₁₃ COOCH ₂ CHOHCH ₂ OH	30	Benzene	15
<i>n</i> -C ₁₅ COOCH ₂ CHOHCH ₂ OH	30	Benzene	15
<i>n</i> -C ₁₅ COOCH ₂ CHOHCH ₂ OH	30	Cl-benzene	9
<i>n</i> -C ₁₇ COOCH ₂ CHOHCH ₂ OH	30	Benzene	11
<i>n</i> -C ₁₇ COOCH ₂ CHOHCH ₂ OH	30	Cl-benzene	3–4
<i>n</i> -C ₁₂ H ₂₅ (OCH ₂ CH ₂) ₄ OH	25	Benzene	40–50
<i>n</i> -C ₁₃ H ₂₇ O(CH ₂ CH ₂) ₆ OH	25	Benzene	70–80
Lecithin	25	Benzene	73
Lecithin	40	Benzene	55
Li ⁺ Phenyl stearate	25	Benzene	20
Na ⁺ Phenyl stearate	25	Benzene	25
K ⁺ Phenyl stearate	25	Benzene	22
<i>n</i> -C ₁₂ H ₂₅ NH ₃ ⁺ C ₂ H ₅ COO [−]	25	Benzene	2
<i>n</i> -C ₁₂ H ₂₅ NH ₃ ⁺ C ₃ H ₇ COO [−]	25	Benzene	6
<i>n</i> -C ₁₂ H ₂₅ NH ₃ ⁺ C ₃ H ₇ COO [−]	25	Cyclohexane	3
<i>n</i> -C ₁₂ H ₂₅ NH ₃ ⁺ C ₃ H ₇ COO [−]	25	CCl ₄	10
Na ⁺ di-2-Ethylhexylsulfosuccinate	30	Dodecane	32
Na ⁺ di-2-Ethylhexylsulfosuccinate	30	Cyclohexane	32
Na ⁺ di-2-Ethylhexylsulfosuccinate	30	Benzene	32
(<i>n</i> -C ₇ COO [−]) ₂ Zn ²⁺	—	Toluene	6
(<i>n</i> -C ₉ COO [−]) ₂ Zn ²⁺	—	Toluene	5
(<i>n</i> -C ₁₁ COO [−]) ₂ Zn ²⁺	—	Toluene	4
Na ⁺ Dinonylnaphthalenesulfonate	25	Benzene	10
Li ⁺ Dinonylnaphthalenesulfonate	25	Cyclohexane	8

The effect of the hydrocarbon tail length in a homologous series of surfactants was found to be relatively small when compared to that in water. It was shown, however, that the aggregation numbers of the micelles decreased as the carbon number increased for a series of quaternary ammonium halides and metal carboxylates.

The presence of small amounts of water in a nonaqueous surfactant environment can have a significant effect on some systems. Particularly large effects have been found in solutions of sodium di-2-ethylhexylsulfosuccinate in toluene and phenyl stearate soaps in benzene. It can be presumed that the effects of water and other impurities on nonaqueous micelle formation stem from alterations in the dipolar interactions between head groups induced by the additive or impurity. Although **cmc** values for a number of systems are listed in Table 6.21, the uncertainties associated with the

nature of the aggregation process and of the aggregated species make a lengthy discussion of the type given for the aqueous systems complicated and somewhat more speculative than aqueous systems. That is not to say, however, that such phenomena are not theoretically and practically important. While micellization process occurs in water the, with some exceptions, over a fairly limited concentration range, the same is not always true for the nonaqueous process (Table 6.22). Solution physical properties that are measured to determine micelle formation often undergo a smooth, continuous transition over several orders of magnitude in concentration. As a result, the designation of a given concentration as the **cmc** may become more a matter of the judgment of the investigator than the sensitivity of the technique. The same potential problems are present in aqueous systems, of course, but experience has shown them to be of only minor significance when due care is taken in the experiments.

A fact of life in many aspects of life in the sciences is that many times things are not as simple as they appear from the “distance” of limited experimental data. Chapter 14 presents some information about some newer, in the sense of being less well known, types of surfactants that often break the rules given above with respect to surface activity, micellization, and similar phenomena in terms of activity–chemical structure. But that is what makes science challenging and fun.

7

Beyond Micelles

Higher Level Self-Assembled Aggregate Structures

Chapter 6 discussed the formation of relatively simple, if that term can be used in this context, small, uniform, or isotropic self-assembled association structures or micelles in dilute surfactant solutions. We know, however, that surfactants and other amphiphilic molecules, including naturally occurring lipids, some proteins, and a variety of combined natural chemical species tend to associate into structures more extensive than “simple” micelles in both aqueous and nonaqueous environments. In many cases, such assemblies can transform from one type to another as a result of sometimes subtle changes in solution conditions such as (i) changes in the concentration of the amphiphilic components, (ii) the addition of new surface-active components, (iii) changes in solvent composition, (iv) the addition of electrolytes or other solutes, (v) temperature changes, (vi) changes in solution pH, and (vii) unspecified influences from internal and external sources – such as the phase of the moon, or so it seems at times.

The basic concepts that govern surfactant self-association or aggregation into micelles discussed previously also apply to the formation of larger, more extended aggregate systems. Such higher systems may be generally divided into “intermediate” and “bicontinuous” structures. The intermediate structures may be defined roughly as normal two-phase systems including liquid crystals, vesicles, bilayers, membranes, and microemulsions. In this chapter, attention will center on essentially two component surfactant and water systems. In the real world, however, three or more component systems are those of most technological and academic interest. The inclusion of microemulsions in the category of self-assembled aggregate structures is warranted by the fact that they fit the definition of self-assembly.

Historically, microemulsions were discussed as a separate family of colloids that form essentially spontaneously and are thermodynamically stable. However, microemulsions must, by definition, contain at least three components – solvent, amphiphile, and dispersed phase – and quite often contain a fourth, the so-called cosolvent. Recent experimental and theoretical work has tended to move them into the larger family of surfactant aggregates, their complex composition notwithstanding. That convention will be followed here, although there still remain a number of points of contention that need to be resolved on their classification as surfactant mesophases on a par with classical liquid crystals.

7.1 The Importance of Surfactant Phase Information

In physical chemistry and related areas, a phase diagram is a type of graph used to indicate the conditions of temperature, pressure, volume, etc. at which distinct thermodynamically stable phases of a compound or a mixture can occur and coexist at equilibrium. Although they are usually

not very well understood or even considered in many if not most areas of chemistry, they can be very useful for understanding the solution behavior of materials in important industrial and technological applications. One of the areas in which phase diagrams can be revealing is the study of surfactants and other amphiphiles. The construction and interpretation of phase diagrams are notoriously tedious and fraught with pitfalls, especially when applied to industrial surfactants whose compositions can be somewhat ill defined. For that reason, along with a probable lack of attention at the basic level, the potential utility of such information is quite often overlooked in the general course of a chemical education. That can be a potentially unfortunate situation, however, since phase information can represent some of the most useful physical data for determining the function and utility of surfactants and other materials in important applications. Most often, however, the trial-and-error method of studying surfactant solution is the preferred approach.

As an example, the physical behavior of the components in a physical or chemical process will almost certainly change with changes in the temperature, concentration, and chemical composition of the process mixture. Changes in viscosity, among other characteristics, will usually accompany changes in process temperature, as will changes in solvent concentration. Prior knowledge of what changes can be expected, and how they might affect the overall process can be important for process engineers in finalizing process designs. The same can be said about the application of surfactants in many industrial processes.

At the chemical level, where process reactions depend critically on the chemical potentials of reactants, a phase change for one or more components may be accompanied by a change in reaction rates, impacting the apparent kinetics of a process for reasons other than strictly chemical reactivity. That is, the phase change may result in a misinterpretation of the chemistry of the process.

Many industrial separation technologies also rely on accurate knowledge of phases. One of the oldest chemical technologies, soap making, depends directly on recognizing and inducing phase changes in order to obtain the desired product characteristics. The refining of fats also relies on the controlled precipitation of amphiphilic materials.

Detailed phase data provide a complete description of the solubility of surfactants and other amphiphiles. Such data can be important in the selection and design of complex systems involving surfactant activity. A surfactant candidate, seemingly interesting for economic reasons, for example, may be found to be inappropriate under some conditions if a complete understanding of its phase data is available, and time and money thus saved. If such data were not available, the surfactant failure could possibly become apparent later in the development process resulting in a very expensive reengineering process.

The optimum functioning of some surfactants, such as in foams and emulsions to be discussed in later chapters, has been found to depend on the phase behavior of the surfactant in the interfacial region. Foam stability, for example, has been correlated with the presence of more than one surfactant phase, a small amount of a liquid crystalline phase significantly improving the stability of the system.

Finally, although most industrial surfactants are really mixtures of a homologous series of hydrophobic groups, and for nonionic materials the hydrophilic group as well, a quantitative chemical analysis of the actual composition of nominally identical materials from batch to batch represents a significant task. The phase behavior of surfactants has been found to be so sensitive to the characters of both the head and tail groups that significant deviations or differences can be relatively easily detected from the phase behavior of the material relative to a control material. In fact, phase behavior can be used as an analytical tool to differentiate surfactants from non-surfactant amphiphiles.

However, notwithstanding the potential importance of phase diagrams in many applications, a detailed venture into the topic is well beyond the scope of this work. Some more information about specific surfactant systems will be presented as special topics in Chapter 13.

7.2 Amphiphilic Fluids

In some areas of research and technology, the term “amphiphilic fluids” is used with reference to multicomponent intermediate and bicontinuous aggregate systems. While the terminology is not “classical” in surface science, it is useful in terms of our new knowledge and understanding of complex systems containing amphiphilic materials. Systems falling into the category of amphiphilic fluids not only are important in physical chemistry but also form the basis of our understanding of structural biology. They have even inserted themselves into the fields of “soft” matter physics and materials science from both fundamental and practical perspectives. Their applications are also widespread, encompassing, for example, the actions of detergents in mammalian respiration. Cell membranes, we know, are complex macromolecular assemblies of, in large part, self-assembled phospholipids and associated protein and glycoprotein molecules.

Application of the concepts of higher-order amphiphilic self-assembled structures is not always as obvious in the more complex systems described here as one would like. At times it requires what seems to be a leap of faith, if such things are allowed in science, to get from a simple micelle to the complex structures to be discussed. This chapter presents some of the general aspects of the larger aggregate structures formed spontaneously by surfactants and other amphiphilic species that may not technically be surfactants, but exhibit many of the same solution characteristics. The discussion is not meant to be comprehensive but rather is intended to introduce some basic concepts along with some images that will help the reader grasp some of the why’s and how’s of the processes involved. With a basic conceptual understanding, the potential user will hopefully be in a position to delve deeper into the menagerie of molecular aggregation processes in the search for a solution to his/her needs.

7.2.1 Liquid Crystalline, Bicontinuous, and Microemulsion Structures

The selective chemical affinity between the parts of a surfactant molecule or other amphiphiles and the solvent or other components of a mixture is the driving mechanism responsible for aggregate structure formation. After decades of study, higher-order self-assembled surfactant and lipid structures continue to present a number of theoretical and experimental questions. Although this chapter presents some of the more fundamental principles and unresolved issues surrounding lyotropic self-assembly in equilibrium, the literature is far too extensive to be treated adequately here. Attention is focused on observations related to the more classical “intermediate” phases of complex aggregate structures. More involved membrane fusion intermediates and developments in the theory of phase stability of mesh, sponge, and cubic bicontinuous structures only be addressed briefly. Also, generally excluded are geometrically deformed hexagonal phases, such as the so-called rectangular “ribbon” intermediates. The interested reader is referred to the works cited in the Bibliography for more details.

Micellar, lamellar, rodlike (usually hexagonal), mesh, and bicontinuous mesophases can form structured, equilibrium phases, in addition to the more “disordered” mesophases now generally recognized to be dominated by microemulsions and, more recently, the so-called sponge mesophases. Theoretically, recent advances in the understanding of lyotropic self-assembly have come

about through the fusion of thermodynamics and molecular geometry (see Chapter 6) that in turn evolved from earlier concepts such as the classical hydrophile–lipophile balance (HLB) and related principles of hydrophobic interactions. Newer, more complete theories explain observations on the more complex and rigid systems based on the concept of membrane packing and bending energy as the dominating factors in the self-assembly process.

A great deal of the interest and activity in self-assembly processes today goes beyond the classical studies of equilibrium aggregation and phase studies, with a great deal of effort being devoted to such dynamic features as solution rheology and phase transformation kinetics. Application studies also look toward the synthesis of novel meso-structured inorganic materials using lyotropic systems as templates. Nevertheless, it is still important to increase our understanding of near-equilibrium self-assembly processes, since they are fundamental to understanding nonequilibrium, dynamic processes in amphiphilic systems and impact so many other fields, particularly the development of new materials and systems, and membrane function and fusion in biological systems.

The experimental and theoretical study of mesophase formation in amphiphilic systems emphasizes the basic chemical, physical, and materials science aspects of the systems. The most commonly discussed mesophases, beyond the simple micelles discussed in Chapter 6, are lamellar, aggregated micellar (packed in various cubic and hexagonal close-packed arrays), columnar or ribbon phases (rod-shaped micelles stacked in a two dimensional hexagonal or rectangular array), microemulsions, and the cubic bicontinuous mesophases. The experimental techniques normally used to identify these mesophases are NMR line shape analysis, diffusion measurements, small-angle neutron and X-ray scattering, and optical texture analyses. In addition, reconstruction of electron density profiles and very low-temperature transmission electron microscopy (TEM) have been used to elucidate the details of these meso-structures.

The current theoretical understanding of these structures is based on the combined concepts of a preferred molecular shape and a preferred membrane curvature resulting from basic molecular geometry considerations. In essence, it is assumed that deviations from a preferred shape or curvature result in an increase in bending energy, and the resulting membrane or aggregate shapes are the result of the minimization of that energy.

Taking a spring as a conceptual model, there will be an equilibrium or rest configuration that represents an energy minimum that is determined by the chemical composition of the spring and the history of its formation. If that rest configuration is distorted by compression, extension, or bending, a restoring force or energy is introduced that will, if possible, restore the spring to its rest state. If the distortion becomes excessive, the spring may become permanently distorted (e.g. develop a new rest configuration) or break completely (Figure 7.1).

A similar effect is invoked for amphiphilic membranes in that they will have a rest state, or curvature in this case, that is determined by the geometric packing requirements of the constituent molecules that will try to maintain the minimum energy state. If the membrane is distorted, the packing energy of constituents will try to force the membranes back into its minimum energy state. Like the spring, if the restoring capacity of the membrane structure is exceeded or if a component modification changes the net energy of the system, irreversible membrane rupture may occur. In biological systems, such rupture may be involved in such vital processes as cell division and the entry and expulsion of specific components such as ions, hormones, enzymes, etc. It may also be involved in unwanted activities such as the penetration of viruses or toxins into target cells.

Interfaces formed by amphiphilic molecules can take on three configurations: (i) they can be curved toward the hydrophobic region of the molecule, a conformation usually referred to as Type 1 curvature; (ii) they can curve toward the polar or hydrophilic region, the Type 2 curvature; (iii) or they can be essentially planar. The three basic categories are illustrated in Figure 7.2.

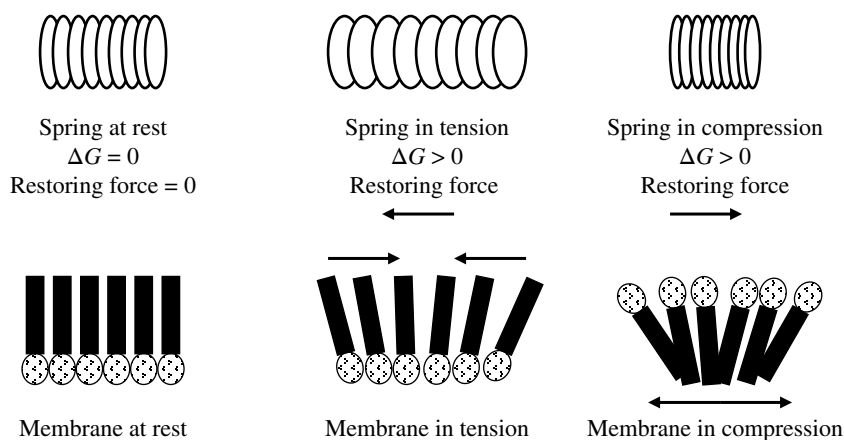


Figure 7.1 A spring model of membranes and related packing and bending energy characteristics.

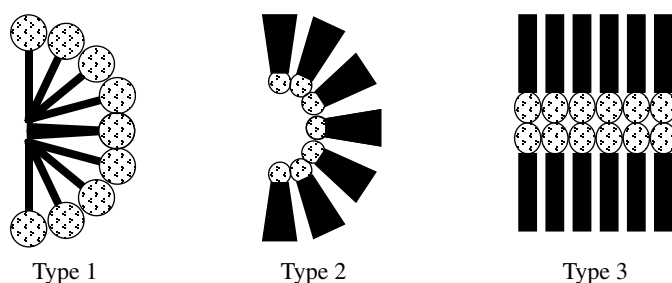


Figure 7.2 The three basic “senses” of curvature of amphiphilic interfaces and membranes.

The effect of molecular geometry on the probable aggregation structures of amphiphiles was introduced in Chapter 6. As indicated, Type 1 curvature is favored by amphiphiles for which the head group, S , is relatively bulkier than the average cross-sectional area of the tail, R , such as single-chain charged detergents. Type 2 is favored by molecules with bulky hydrophobic chain regions, such as double-chain surfactants or single-chain materials in high salt solution, which will reduce the “effective” size of a polar head group. Planar, or approximately so, assemblies are found for particular situations in which the volumes of the head group and hydrophobic tail are essentially equal or balanced. In terms of the geometric analysis introduced in Chapter 6, the critical packing parameter for the system is essentially unity. Most biological lipids, for example, must be delicately balanced in their hydrophobic–hydrophilic geometries, so that their phase diagrams at biologically relevant physical conditions favor almost flat or planar lamellar mesophases, since cell membranes require such structures for cell integrity and function. In a real system, however, the concept of a well-defined defect-free, planar lamellar state is an idealization, and such systems are usually delicately balanced and ready for transformation from one curved type to the other as required by the proper functioning of the system.

7.2.2 “Classical” Liquid Crystals

The spontaneous formation of surfactant aggregate structures or micelles at relatively low concentrations opens the door to a veritable “zoo” of larger, more structurally complex, and certainly

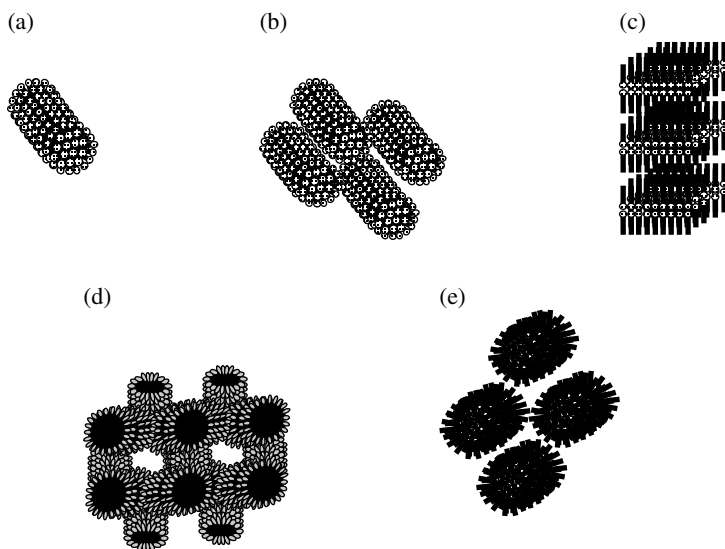


Figure 7.3 Schematic structures of some of the principal mesophases of amphiphiles: (a) rod-shaped micelles, (b) hexagonal close-packed rods, (c) bilayer or multi-layer sheets, (d) a cubic bicontinuous phase, and (e) reversed hexagonal rods.

more theoretically complex self-assembled structures that inhabit our natural world and make life as we know it possible. While the concepts presented in Chapter 6 to explain micelle formation in aqueous and nonaqueous solutions are relatively straightforward, chemically speaking, it should be obvious that there is a great deal of room for complications to set in as a system becomes more complex.

Simple micellar systems may be characterized generally as being dilute isotropic phases that show little structure beyond that of the localized micellar aggregate. That definition is a bit tenuous, however, since the broad spectrum of aggregate structures (Figure 7.3) can be continuous from the “simple” spherical, ellipsoidal, and disk micelles through the larger, intermediate non-isotropic structures such as liquid crystals, bicontinuous mesophases, vesicles, microemulsions, and extended membranes already mentioned. Transitions between such structures can result from subtle changes in amphiphile concentration, electrolyte concentration and pH changes, nonionic solute addition, temperature changes, etc. This chapter introduces some of the structures and properties of the so-called lyotropic mesophases that may be present in more concentrated surfactant solutions. The subject of surfactant phase behavior is quite complex and has been reviewed in various publications cited in the Bibliography. The discussion here is limited to a general descriptive introduction to water-based systems. The possible role of mesophases in various surfactant applications will be mentioned in the appropriate chapters.

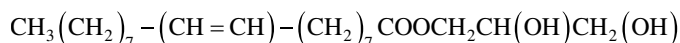
7.2.3 Liquid Crystalline Phases in Simple Binary Systems

It has been recognized for many years that surfactant solutions with concentrations well above the critical micelle concentration can exhibit physical properties that indicate the presence of various degrees of structure above the “simple” micellar level. Such structure formation may be manifested in bulk by abrupt changes in viscosity, conductivity, and other transport phenomena, birefringence, the existence of characteristic X-ray diffraction and radiation scattering patterns, or

spectroscopic analyses. As the surfactant concentration is increased, changes in the physical characteristics of the solution signal corresponding changes in the nature of the aggregated solute as illustrated in Figure 7.2.

We know that the existence of mesophases in aqueous solutions of pure or reasonably homogeneous surfactants is a direct result of the nature of water–surfactant interactions. As the amount of solvent available between the simple dilute solution micelles decreases, interactions between adjacent structures increase to the point that a form of “second phase” coalescence can be invoked, leading to formation of larger disk-shaped or cylindrical micelles (Figure 7.3a). As the concentration process continues, hexagonal close-packed arrays of cylinders may appear (Figure 7.3b) producing the hexagonal or normal middle phase. The next step in the process is the coalescence of the adjacent, mutually parallel cylinders to produce the neat phase, characterized by lamellar bilayer structures separated by solvent phases (Figure 7.3c). Under some circumstances, especially in the presence of nonaqueous solvents, a reversed hexagonal phase will appear that contains close-packed cylindrical arrays but with the internal region of the cylinders containing the aqueous phase (Figure 7.3d). Such structures not only are generally termed cubic bicontinuous phases but also are referred to as “cubosomes.”

Cubosomes are discrete, submicron, nanostructures formed in a cubic bicontinuous liquid crystalline phase. The term “bicontinuous” refers to the presence of two distinct hydrophilic regions separated by the bilayer structure of the amphiphilic phase. They are an interesting topic for research, especially in the pharmaceutical and medical areas because their unique structures provide interesting possibilities for controlled release drug applications. A number of surfactant species that have the ability to form such structures under the proper conditions have been studied. One of the most studied is glycerol monooleate or “monoolein.”



The potential nano-vehicles are generated from a self-assembled lipid mixture and studied by means of high-resolution cryogenic transmission electron microscopy (cryo-TEM). Such structures have been identified in naturally occurring structures such as stressed cells and mitochondrial membranes. They are formed at controlled temperatures into bilayers twisted into three dimensions with a minimal surface forming a tightly packed structure with bicontinuous domains of water and amphiphile. Three possible cubic structures have been suggested. The variation in structure suggest that cubosomes can be very effective drug delivery system due to their ability to protect the integrity of the ingredients they transport. The uses of cubosomes are still being researched, but they range from systems for efficient drug delivery into specific body systems. They are also under active investigation as templates for producing and stabilizing palladium and other types of nanoparticles.

In most fluids and some homogeneous solids, diffusion is “isotropic” in that it is the same in all directions with the same diffusion coefficient. This property gives cubosomes the ability to be used in highly structured biological tissues that often exhibit different diffusion coefficients in different directions or “anisotropic diffusion.” Because of advantages such as the unique structure of the cubic phase and its resemblance to biological membranes, as well as the biodegradability of many amphiphiles that form cubosomes structures, they represent a good potential mechanism for drug delivery systems. In addition, the tortuous pathway a solute must traverse in such systems serves to slow down typical diffusion rates. The ability of cubosomes to incorporate hydrophilic, hydrophobic, and additional amphiphilic materials, their relative ease of preparation, and the unique characteristics mentioned make them seem ideal vehicles for controlled drug delivery systems.

The conditions of temperature and concentration that produce the various solution phases in surfactant–solvent systems can be determined (with a great deal of laboratory work) by the construction of phase diagrams. The construction and interpretation of such diagrams is a complex undertaking, which is beyond the scope of this work. However, sufficient literature exists to permit certain generalizations that will help in understanding the activity of most reasonably simple surfactant systems.

Most of the published work on the phase behavior of anionic surfactants has dealt with the simple carboxylic acid soaps, with less information available on the sulfates, sulfonates, etc. It is generally found, however, that certain trends hold over a wide range of products so that one can predict events with some degree of confidence.

For a typical anionic surfactant, the micelles remain approximately spherical or ellipsoidal over a substantial concentration range above the **cmc**, but ultimately, they become rodlike as the concentration continues to increase. At concentrations in the range of 20–30% by weight, a new phase normally appears that is birefringent and quite viscous. X-ray diffraction studies show that this phase consists of many long, parallel, rodlike aggregates arranged as illustrated in Figure 7.3b. The aggregate interiors are apparently rather fluid, resembling liquid hydrocarbon in many respects. This phase is what is classically referred to as a liquid crystal in that it possesses a substantial degree of order in at least one dimension while not being truly crystalline. As indicated previously, the usual terminology for such a structure is the normal hexagonal or simply the hexagonal phase. In the soap industry it is traditionally referred to as the middle phase.

As the surfactant concentration continues to increase, it may become energetically favorable for the surfactant molecules to arrange themselves into a bilayer structure, the lamellar phase (the “neat” phase to the soap maker) (Figure 7.3c). Continuation of the process of increasing the surfactant concentration may lead to the formation of the reversed or inverted hexagonal phase, which again involves an array of rodlike aggregates, but now with the rod interiors being the aqueous phase (Figure 7.3d). It is in the region of transition between the normal and the reversed hexagonal phases that the cubic bicontinuous phase appears.

In terms of surfactant structure, one can expect that a more hydrophilic head group will tend to delay the formation of the hexagonal and subsequent mesophases as a result of charge repulsion among adjacent molecules in the micelle. While the effect of changes in counterion will usually be small, if a significant degree of ion binding occurs for a given head group, thereby reducing its hydrophilicity, one can expect the appearance of the hexagonal phase at lower surfactant concentration. Within a homologous series, it is generally found that the appearance of the liquid crystalline phases will occur at lower concentrations for higher members of the series, paralleling the normally observed decrease in **cmc**.

Much less work has been reported on the phase behavior of cationic surfactants. In general, the phase diagrams for simple quaternary ammonium halides closely resemble those of anionic surfactants. In some cases, it has been found that the phase behavior of such materials is much more sensitive to counterion effects than anionic species.

Dodecyl trimethylammonium chloride in water, for example, shows the presence of two distinct viscous isotropic cubic phases at room temperature. Similar results are found for the decyl and tetradecyl analogues, while the hexadecyl and octadecyl members of the series do not exhibit these phases. The cubic phases are apparently absent in the corresponding bromides of all members of the series.

For a nonionic surfactant of the polyoxyethylene class, the situation is more complex. In a relatively pure sample of such a surfactant, one may encounter not only the usual hexagonal and lamellar phases but also one or more isotropic liquid phases. It may be that such phases contain disk-shaped micelles resulting from disruption of the extended lamellar phase by the large steric

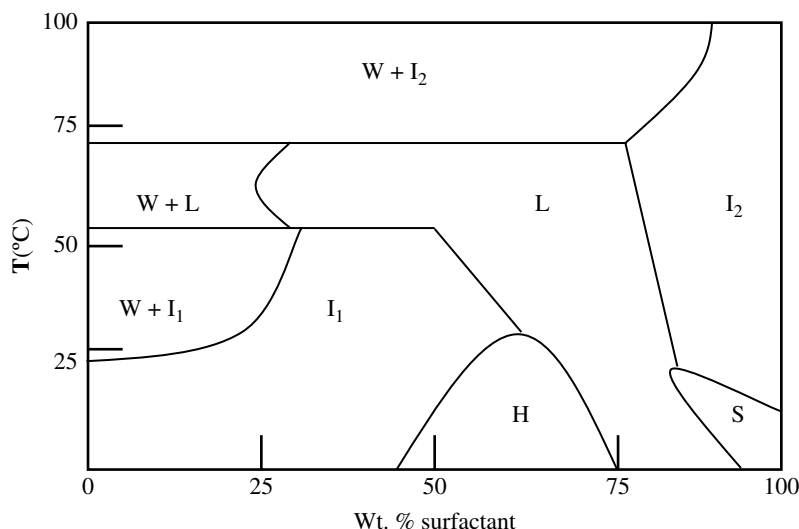


Figure 7.4 Schematic representation of a typically complex phase diagram for a nonionic POE surfactant (W: water, H: hexagonal, L: lamellar, I_1 and I_2 : isotropic phases, S: solid), in which phase I_1 would normally be a micellar solution.

requirements of the hydrated POE head group. Similar effects have been reported for anionic surfactants at sufficiently high electrolyte concentrations or in the presence of oil-soluble alcohols. In those cases, some form of association phenomena (ion binding and/or some form of molecular complex formation, for example) might be involved.

In general, the phase behavior of a POE nonionic surfactant (Figure 7.4) is more sensitive to surfactant structure than in the ionic case. Since the vast majority of such materials are, in fact, mixtures of POE chains of various lengths, phase diagrams lose a great deal of their theoretical utility, even though they may still be useful from a practical standpoint. While reproducible results can be obtained for a given sample of surfactant, another material of nominally the same structure may produce different results due to differences in POE chain distributions. As a result, it is not always a safe practice to extrapolate results for one sample to another of nominally the same material, even that provided by the same manufacturer.

Not surprisingly, in nonionic systems temperature can have a much greater effect on phase behavior than in ionic materials. As the temperature of a solution of the nonionic surfactant is increased, the concentration at which the hexagonal phase appears decreases, as does the concentration at which transformation from hexagonal to lamellar occurs. Because the POE surfactant is solubilized in water by hydration of the POE links, the higher temperature reduces the degree of hydration at a given concentration, reducing the effective size of the POE group and facilitating the formation of the lamellar aggregate. The cloud point for the nonionic surfactant will lie at the upper boundary of the liquid isotropic phase for a given surfactant concentration.

It may be noted that the changes in a surfactant system that lead to liquid crystal transformation appear to go hand in hand with changes that affect the size or hydrophilicity of the head group, that is, changes in hydration, changes in the degree of counterion binding, electrical charge screening, etc. It will be remembered from Chapter 6 that the same factors are found to effect changes in simple micellar solutions. In summary, changes that reduce the effective area of the head group cause the system to tend away from spherical aggregates and toward cylinders, lamellar structures, and reversed micelles.

7.3 Temperature and Additive Effects on Phase Behavior

The particular aggregate phase of an amphiphilic material present at a particular concentration will depend on molecular structure, temperature, ionic strength of the aqueous phase, and the presence or absence of other solutes, especially other weakly surface-active materials such as esters, amides, and alcohols. For a typical anionic surfactant, an increase in temperature will usually increase the surfactant concentration at which the hexagonal phase appears. This reflects the increased solubility of the monomeric surfactant, the higher **cmc**, and the greater thermal mobility and solubility of the hydrophobic tail. An increase in ionic strength of the solution will generally have the opposite effect; that is, the hexagonal phase will appear at lower concentration.

A simplified explanation for those observations is that the increased ionic strength reduces the charge repulsion between adjacent head groups, facilitating the closer packing of molecules into the rodlike aggregates. In effect, the surface area requirements of the head group are reduced, leading to the effect predicted by geometric considerations discussed in Chapter 6. A similar explanation has been invoked for the effect of low concentrations of short-chain alcohols. The nonionic species can pack between the larger surfactant molecules, decreasing the effective dielectric constant of solution in the area of the charged groups and serving to insulate somewhat the neighboring charges, permitting higher packing densities and the transition to aggregate structures with a smaller radius of curvature.

More hydrophobic additives such as free fatty acids and their esters and amides, long-chain monohydric alcohols, and nitriles may have an even more dramatic effect on the phase behavior of a surfactant due to solubilization phenomena. The general subject of solubilization in micellar systems is discussed in Chapter 8. For now, we will focus on the effects the presence of solubilized materials may have on liquid crystal phases.

Four main classes of solutes affecting liquid crystal phases can be defined based on the overall nature of the additive. These are the completely hydrophobic materials, such as hydrocarbons and halogenated hydrocarbons; weakly surface-active materials, such as nitriles, methyl esters, ketones, and aldehydes; slightly more surface-active monohydric alcohols; and fatty acids. As one might expect, each class has a distinct effect on the phase transitions in a ternary surfactant system.

For hydrophobic additives, one generally finds that an increase in the relative concentration of the additive results in an increase in the range over which one encounters liquid isotropic and middle phases, leading ultimately to a viscous isotropic mesophase. When the additive possesses a slightly polar group (ester, amide, etc.), the solubilizing capacity of both the liquid isotropic and middle phases may be increased significantly, resulting in the formation of a lamellar neat phase at high additive concentrations.

When the additive is a monohydric alcohol, a much more complex system may be encountered, often with the formation of the lamellar neat phase at much higher water concentrations than normal. It is also common to find a second liquid isotropic phase in which the alcohol becomes a secondary solvent. Additional complex mesophases of indefinite structure may arise, leading ultimately to a reversed middle phase. In the presence of fatty acids, the phase diagram will resemble that of the monohydric alcohols except that the liquid isotropic solution in the acid will usually be found to incorporate more water.

Obviously, the phase behavior of a surfactant is a complex matter that may significantly affect its activity in a given application. While the discussion above is highly abbreviated, it should serve to illustrate again the great importance surfactant structure and environment can have in complex (and sometimes simple) systems.

7.4 Some Current Theoretical Analyses of Novel Mesophases

The attractive, simple picture of amphiphilic aggregation structures is, as already noted, often blurred by reality. The classical method for studying the phase behavior of surfactants has been through the construction of phase diagrams – a delicate and laborious process that requires care and dedication (read “many ready and willing graduate or undergraduate hands”). Even then, the interpretation and application of the results to predictive theory requires care, knowledge, intuition, and significant mathematical ability (and computer power). In practice, it is still not possible to accurately predict a phase diagram from the molecular composition and structure of an amphiphile alone. That goal is so far beyond our reach, in part, because we still do not understand the finer points of such factors as specific ion effects governing the delicate balance of water–hydrophobe or electrostatic and dispersion force interactions at the molecular level. Neither do we have a really good grasp of membrane rheology – bending elastic moduli and undulation forces, for example – or entropic contributions that predominate in the self-assembly process. The basic problem remains the impossibility of deducing a complete theoretical phase diagram from first principles, even for a simple model amphiphile. The problem lies in the impossibility of writing down a complete Boltzmann-type distribution of all possible membrane geometries and topologies, appropriately weighted by their energies and entropies.

An important question in the analysis of mesophase structures is that of the relative stabilities of intermediate vs. bicontinuous mesophases. Most analyses of the available data suggest that intermediate mesophases of unusual topologies and geometries fall into three topological classes: non-cubic bicontinuous sponges, branched bilayers, and punctured bilayers. A fourth possible class, “ribbon” mesophases, consists of geometrical distortions of columnar micelles in hexagonal mesophases. Experimental studies of surfactant–water phase diagrams suggest that intermediate structures form in place of bicontinuous cubic mesophases once the surfactant chains exceed a certain length or their rigidity is enhanced, such as by replacing hydrocarbon with fluorocarbon chains.

7.5 Vesicles and Bilayer Membranes

The association of surfactants into relatively simple aggregate structures such as spheres, ellipses, and disks allows a reasonably straightforward analysis of the fundamental aspects of their structure – their kinetics, thermodynamics, geometric considerations, etc. The simplest extension of the simple micellar structures, namely, the rodlike micelles often encountered in systems of ionic surfactants in solutions of high salt content, presents a number of theoretical difficulties. Such structures are large (relative to spherical systems) and polydisperse, with no theoretical limit on the length that can be attained. Their average aggregation number is also very sensitive to the total surfactant concentration, so the properties of the system do not always lend themselves to easy analysis. In general, their unusual properties result from the large dissymmetry in the dimensions of the structural unit and the effects of the ends of the rods, where the associated molecules are forced to pack into hemispherical caps.

As predicted by the geometrical approach to aggregation, amphiphilic materials that cannot readily pack into neat, closed structures such as simple micelles are exactly those that are found to produce larger units such as vesicles and extended bilayers. Such materials will have relatively small head groups, or, as is more common, their hydrophobic groups will be too bulky to be packed in a manner necessary for normal micelle formation. Such a state of affairs is particularly common

for molecules having more than one hydrocarbon chain, very highly branched chains, or structural units that produce molecular geometries incompatible with effective packing into highly curved structures.

Although extended planar bilayers are a thermodynamically favorable option for the association of some bulky surfactants in aqueous solution, there are some conditions under which it is more favorable to form closed bilayer systems, leading to the existence of membranes and vesicles. Such a situation arises from two basic causes: (i) even large, highly extended planar bilayers possess edges along which the hydrocarbon core of the structure must be exposed to an aqueous environment, resulting in an unfavorable energetic situation, and (ii) the formation of an infinitely extended structure is unfavorable from an entropic standpoint. The formation of spherical closed vesicles, then, addresses both those factors: the edge effect is removed by the formation of a closed system, and the formation of structures of finite size overcomes much of the entropic barrier. As long as the curvature of the vesicle is gentle enough to allow the packed molecules to maintain close to their optimum surface area, vesicles will represent viable structures for the association of surfactants and related materials.

Over the years it has been confirmed that geometric factors control the packing of surfactants and lipids into association structures. The concept has already been introduced but warrants repetition in the current context for clarity. The packing propensity of a given amphiphilic structure can be conveniently given by the critical packing parameter, denoted here as P_c , and given by

$$P_c = v / a_o l_c \quad (7.1)$$

where v is the volume of the hydrophobic portion of the molecule, a_o is the optimum head group area, and l_c is the critical length of the hydrophobic tail, effectively the maximum extent to which the chain can be stretched out, subject to the restrictions of bond lengths and bond angles. The value of P_c will determine the type of association structure formed in each case. A summary of the structures to be expected from molecules falling into various “critical packing” categories is given in Table 7.1.

Examples will be found in materials that do not fit neatly into such a scheme; the general concepts are usually found to be valid. For surfactants and other amphiphiles that form bilayer

Table 7.1 Expected aggregate characteristics of amphiphiles as determined by their molecular structure and packing parameter, P_c .

General surfactant type	P_c	Expected structure
Simple surfactants with single chains and relatively large head groups	<0.33	Spherical or ellipsoidal micelles
Simple surfactants with relatively small head groups, or ionic materials in the presence of large amounts of electrolyte	0.33–0.5	Relatively large cylindrical or rod-shaped micelles
Double-chain surfactants with large flexible head groups and flexible chains	0.5–1.0	Vesicles and bilayer structures
Double-chain surfactants with small head groups or rigid, immobile chains	1.0	Planar extended bilayers and cubic bicontinuous phases
Double-chain surfactants with small head groups, very large and bulky hydrophobic groups	>1.0	Inverted micelles

structures, several generalizations have been found useful that make it easier to understand the geometric consequences of the structure of the amphiphile.

- 1) Molecules with relatively small head groups, and therefore large values for P_c , will normally form extended bilayers, large (low curvature) vesicles, or inverted micellar structures. Such results can also be brought about in many “normal” anionic systems by changes in pH, high salt concentrations, or the addition of multivalent cations.
- 2) Molecules containing unsaturation, especially multiple *cis*-double bonds, will have smaller values for l_c and thus will tend toward the formation of larger vesicles or inverted structures.
- 3) Multichain molecules held above the melting temperature of the hydrocarbon chain may undergo increased chain motion, allowing *trans*-gauche chain isomerization, reducing the effective value of l_c and resulting in changes in aggregate structures.

These generalizations on assemblies of surfactants and other amphiphilic molecules offer a broad view of the types of structure that may be formed as a result of the self-assembly process. They consider only the fundamental relationships between structure and the geometric characteristics of the molecules involved. Not considered are any effects on the systems that may exist as an indirect result of curvature or other distortions of the molecular packing. The interested reader can obtain more in-depth discussions in the works cited in the Bibliography. The unique characteristics of the bilayer and vesicle assemblies have attracted the attention of scientists in many disciplines for both theoretical and practical reasons. The following brief discussion only skims the surface of what is sure to become an even more interesting and important area of surfactant-related surface science.

7.5.1 Vesicles

Many naturally occurring and synthetic surfactants and phospholipids cannot undergo simple aggregation to form micelles because of the structural characteristics outlined above. When dispersed in water, they will spontaneously form closed layered structures referred to as liposomes or vesicles. Such structures are composed of alternating layers of lipid or surfactant bilayers separated by aqueous layers or compartments arranged in approximately concentric circles (Figure 7.5a). If the spontaneously formed multilayer vesicles are subjected to ultrasound or other vigorous agitation, the complex multilayer structure may be disrupted to produce a single bilayer assembly consisting of a unilamellar vesicle in which a portion of the aqueous phase is encapsulated within the single bilayer membranes (Figure 7.5b). In essence, an assembly resembling a biological cell is produced, although the cell wall is composed of the amphiphilic material without all of the

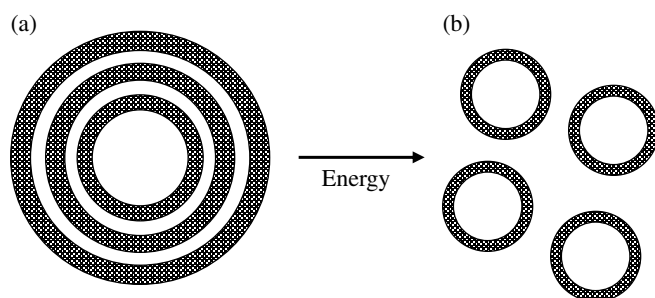


Figure 7.5 Schematic illustration of a multilayer vesicle (a) and single bilayer vesicles (b).

addenda present in biological systems. Typically, a vesicle so produced will have a diameter of between 30 and 100 nm, falling within the size range of classical colloidal systems.

Like biological systems, however, the vesicle is by nature compartmentalized, which makes it amenable to the inclusion of additives in the three phases present: the external aqueous phase, the hydrophobic interior of the bilayer, and the aqueous internal phase. That availability of “carrying capacity” has made vesicles natural candidates as delivery systems in pharmaceutical, cosmetic, and various other industrial applications. Who has not heard of the magical “liposomes” that make the wrinkles of aging disappear? As will be seen below, other “newer” mesophases such as the cubic bicontinuous phase or “cubosomes” already introduced are now beginning to join the corps of amphiphile aggregate workhorses.

Natural and synthetic amphiphiles that form vesicles are, by their nature, of limited solubility in aqueous systems, so the exchange of individual molecules from the bilayer is often relatively slow. In addition, the bilayer structure has a significant degree of internal stability so that vesicles, once formed, can maintain their original structure for a significant amount of time. Lifetimes of from a few days to several months are common, as would be required of systems designed for drug or cosmetics delivery systems. After a period of time, dictated primarily by the composition of the system, the unilamellar vesicles will usually begin to fuse to produce the more complex aggregate structures of the original systems. The rate of that fusion process can be controlled in several ways, including through the proper choice of amphiphile structure, the use of mixed amphiphiles, the addition of non-amphiphilic materials that incorporate into the vesicle wall to provide stability, or the use of amphiphiles with unsaturated hydrocarbon chains that can be subsequently cross-linked or polymerized to “fix” the structure.

As mentioned, one of the interesting and useful characteristics of vesicles is their ability to entrap within the assembly a portion of the aqueous phase present at the time of their formation, along with any solute present at the time. It is then possible to alter the composition of the external aqueous phase after vesicle formation by dialysis, diafiltration, or other related purification techniques. Vesicles, therefore, represent a unique microencapsulating technique. Oil-soluble materials can also be incorporated into vesicle systems, although they would naturally be located inside the hydrophobic portion of the vesicle membrane, like materials solubilized in conventional surfactant micelles (see Chapter 8). The potential for the incorporation of both aqueous and nonaqueous additives into vesicles poses the interesting possibility of producing a system containing two or more active components, one component soluble in the internal water phase, the oil compatible component in the hydrophobic portion of the bilayer, and another in the external aqueous phase, for simultaneous delivery.

Other interesting and potentially useful physical characteristics of conventional vesicles include their potential activity as micro-osmotic membranes; their ability to undergo phase transitions from liquid crystalline to a more fluid state; their permeability to many small molecules and ions, especially protons and hydroxide; and their potential applicability as models for biological membranes.

7.5.2 Polymerized Vesicles

Because of their unique properties, vesicles and related lamellar structures are seen as potentially useful vehicles for various controlled delivery and encapsulation processes and as potential pathways to extremely high-resolution lithographic systems for microelectronics applications, as well as serving as good models for naturally occurring membrane systems. A number of reviews and books published in recent years cover the current state of the art for such applications in great

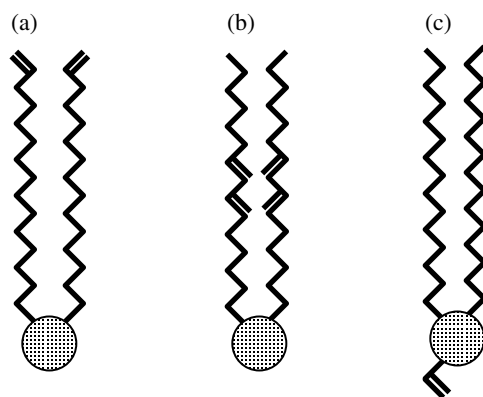
detail. Major barriers to the use of conventional vesicles in such applications include the inherent long-term instability of the systems, their potential for interaction with enzymes and blood lipoproteins, and their susceptibility to the actions of other surface-active materials. The latter effects especially limit the use of vesicles for oral drug delivery, since the bile acids in the digestive tract may lead to a rapid degradation of the amphiphiles, resulting in an undesirably rapid drug release. For such critical applications as controlled release drug delivery, even the most stable systems with a nominal shelf life of several months do not begin to approach the usual requirements of pharmaceutical applications.

As a result of the potential utility and relatively low cost of vesicles, a great deal of effort has been applied to the development of polymerized surfactant and phospholipid systems. Covalently cross-linking the vesicle membrane after the encapsulation process should produce a system in which the basic nature of the vesicle as an encapsulating medium is retained, while the structural integrity and increased stability of a cross-linked polymeric structure are added.

The general approach used to attain such structures has been the synthesis of conventional vesicle-forming amphiphilic materials containing easily polymerizable functionalities in the molecule. After vesicle formation, subsequent polymerization, preferably by some nonintrusive means such as irradiation, produces the final encapsulated system. The polymerizable functionality can be located at the end of the hydrophobic tail, centrally within the tail, or in association with the ionic or polar head group (Figure 7.6). The choice of a preferred structure will be determined by the requirements of the system and the synthetic availability of the desired materials. Drug delivery after polymerization would be regulated by the diffusion rate of the active component through the vesicle membrane or by the rate of membrane breakdown by physiological processes.

Considering the impact of amphiphilic species and aggregated structures in biological systems, it has long been a goal of workers in many allied fields to develop a well-characterized synthetic model of biological membranes. The development of new knowledge and techniques in the areas of vesicles, bilayer and multilayer membranes, cubic bicontinuous phases, and their polymerizable analogues provides new opportunities for research in those areas. Research using model systems may be able to provide answers to questions related to natural processes that have so far eluded the research community because of the complexity and intractability of the natural systems. It may also provide new approaches to the development of new “silver bullet” drugs for the treatment of old problems such as cancer, AIDS, and the like. With time, the skills of human science may finally begin to approach those of nature in producing the systems and processes capable of mimicking and actively modifying biological reality to the benefit of mankind.

Figure 7.6 Typical structures of polymerizable vesicle-forming surfactants: (a) terminal unsaturation in the tail, (b) internal unsaturation in the tail, and (c) unsaturation associated with the head group.



7.6 Biological Membranes

In the past few years, there has been a dramatic increase in interest in the molecular structure of biological membranes. While model systems composed of artificially prepared (or isolated) amphiphilic materials and associated colloids serve a very useful purpose, a better understanding of the reality of biological systems would be invaluable in many areas of biochemistry, medicine, pharmaceuticals, etc. While it is reasonably easy to determine the constituents of a biological membrane, elucidating just how the various components are put together, how they interact, and their exact function within the membrane represents a decidedly more difficult task (Figure 7.7).

New techniques for characterizing the nature of aggregate systems at the colloidal level have opened a wider crack in the door to understanding the finer workings of biological cells and other related structures in life processes. Knowledge gained over the years in terms of cell membrane composition has given way to knowledge of exactly how the various components function as a unit to carry out necessary biological functions.

Aggregated amphiphilic structures in biological systems have been found to include mesh, bicontinuous, and columnar or hexagonal mesophases. Reviews of older data on mesh and bicontinuous mesophases; insights provided by the newer techniques into their relationship to simpler discrete micellar, hexagonal, ribbon, and lamellar phases; and analysis of geometries and topologies have significantly clarified our picture of the how's and why's of biological cell function. The standard picture that has developed proposes a gradual evolution of mean curvature in both Type 1 and Type 2 mesophases within the cell wall that results in the production of a workable system. Those curvatures depend on local conditions such as solvent and solute concentration, specific ion effects (Na^+ vs. Ca^{2+} , for example), temperature to a greater or lesser extent, and the presence of specific “activating” chemicals in the vicinity of the wall membrane.

7.6.1 Some Biological Implications of Mesophases

The biological importance of mesh and other intermediate mesophase structures goes far beyond the finer details of phase studies. Most studies of biological membranes have historically focused on membrane proteins and their influence on biological function. Until recently, that emphasis has been justified by the availability of techniques for the study of protein structure. Newer techniques, however, have made it possible to investigate in depth the equally, or perhaps more important, role of amphiphiles in the control of membrane topology and function. Some significant

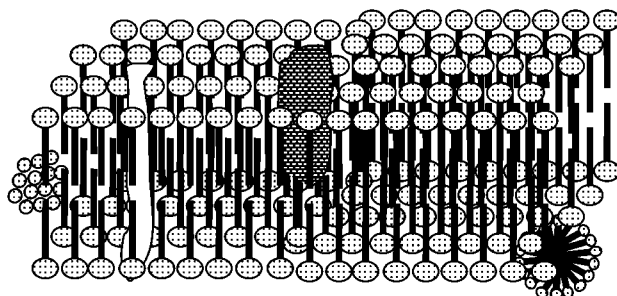


Figure 7.7 A schematic representation of a typical biological membrane including some of the many complex components generally found in such aggregate structures.

experimental results on membrane fusion and dissolution have appeared recently that reinforce suggestions about the importance of lipids in determining membrane form and function.

Direct observations of model physiological lipid membranes using atomic force microscopy (AFM) have shown that carefully prepared bilayers deposited on silicon substrates using Langmuir–Blodgett techniques spontaneously form punctures, tunnels, or channels passing through the structure. Bilayers formed by sequential monolayer deposition (A followed by B), for example, were found to form approximately circular bilayer “punctures,” channels, or defects occupying between 10 and 20% of the membrane area. The spontaneous formation of such “spontaneous” openings traversing the membrane, if they are indeed spontaneously formed, would seem to indicate a natural propensity for the existence of such defects and remind one of the similarities to channels in natural biological membranes used for the transfer of ions and small molecules into and out of the cell interior. The potential relevance of these “defects” to biological membranes is therefore hard to deny.

Low-temperature or cryogenic transmission electron microscopic images of biological membranes also suggest the importance of unusual “intermediate” membrane topologies in biological processes and the possibility of topological and geometric control of membranes by biochemical variations of the bilayer composition. Experiments have been carried out that explore changes in membrane morphology on the addition of surfactants with small shape parameters ($P_c < 1$) to standard bilayer-forming lipids that have $P_c \geq 1$.

More recent work on biologically relevant systems demonstrates the potential importance of studies of amphiphile self-assembly processes. That importance lies in its potential for increasing our understanding of biological functions and their obvious implications. Assuming that the conditions used in the studies do not unduly influence the bilayer structure and has no effect on the activity of the membrane itself, it is becoming clear that membrane-forming lipids found in biological systems can form unusual intermediate (mesh) structures under biologically reasonable constraints. The data suggest a conclusion of major biological importance: punctures or tunnels can form spontaneously and reversibly in lipid bilayer membranes as a result of subtle environmental changes such as the control of water content alone, partially explaining some mechanisms of cellular processes and potentially pointing to new tools and access points for cell manipulation.

The suspicion that biological membrane activity may be controlled by lipids in addition to the conventional protein-governed mechanisms is beginning to be confirmed. That progress in understanding creates a new motivation for the continuation of careful experimental and theoretical study of mesophases in amphiphilic systems. The full class picture of possible mesophases and structures available for self-assembly processes remains to be taken. Further work is required to clarify the balance between protein and lipid activities as the principle functional controls for biological systems. The classic picture of lipids as passive bricks in the membrane wall, supporting the real bio-machinery in the form of proteins and glycoproteins, will need to be retaken, with a better appreciation of the active role of lipids and other membrane-bound agents.

7.6.2 Membrane Surfactants and Lipids

The surface-active components of biological membranes are referred to as lipids, with the majority consisting of double-chain phospholipids or glycolipids. The hydrophobic tails normally contain chains of 16–18 carbons, with one generally being unsaturated. Those structural features immediately indicate that such amphiphiles will have values of $P_c \cong 1$. Those factors guarantee that the lipids will have significant surface activity and will spontaneously form self-assembled bilayer

membranes that can encapsulate or isolate different regions and functions in biological systems (as vesicles, for example), or influence the curvature and conformation of membranes when incorporated into the overall structure. In addition, the long-chain lengths ensure that such lipids will have relatively low solubility in water (as the monomer) and a low **cmc**, and therefore their assemblies will be stable and remain intact while contacting surrounding fluids. The presence of unsaturation in the hydrocarbon chains also helps guarantee that the structures they comprise will remain relatively fluid and flexible over a wide, biologically relevant temperature range. In that way, their chemical composition helps to ensure the functional viability of the biological structure and the organism of which it is a part under varied environmental conditions.

Size, structure, and fluidity of membrane lipids are also important characteristics because those aspects of the amphiphilic molecules make it possible for them to efficiently pack into a variety of bilayer membrane structures with various degrees of curvature and flexibility. That flexibility makes possible the inclusion of other important components of the cell wall including proteins, glycoproteins, cholesterol, etc.

In terms of molecular geometry, one can visualize a mixed amphiphilic system in which one class of lipid having a $P_c < 1$, which will produce a truncated cone shape (Figure 7.8a), while

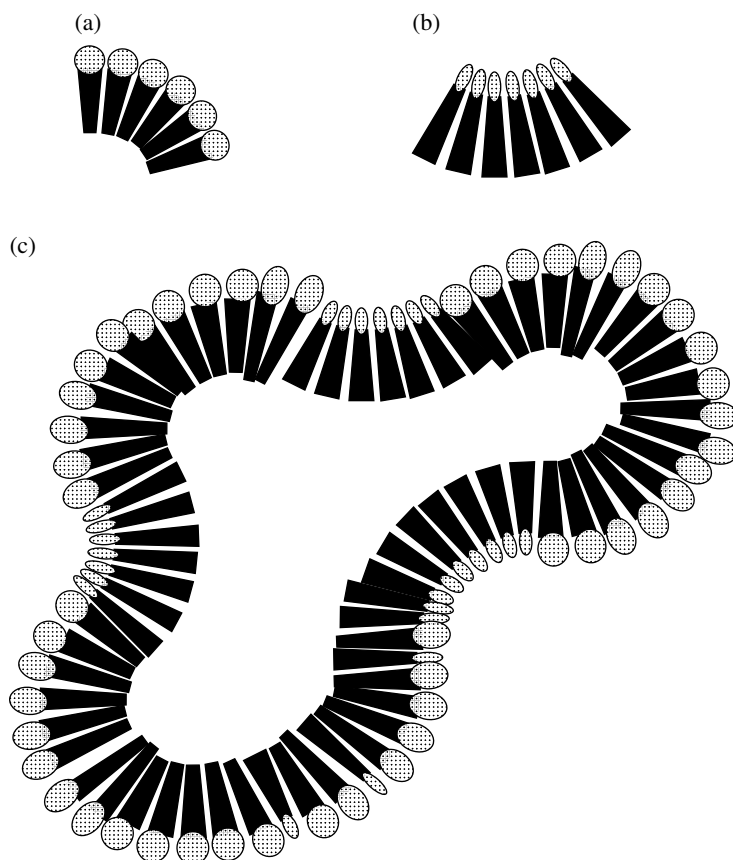


Figure 7.8 Illustration of the role of surfactant molecular geometry in the packing of lipids to form micelles, membranes, and complex cellular structures: (a) a spherical micelle, (b) a reversed micelle, and (c) mixed packing to form planar and cellular structures.

another will have $P_c > 1$ for an inverted truncated cone (Figure 7.8b). Combinations of the two can then accommodate the inclusion of, for example, proteins and cholesterol while maintaining an overall planar structure (or a given degree of curvature) or increase curvature to produce a smaller associated unit. The situation is shown schematically in Figure 7.8c.

Biological membranes, like micelles and vesicles, are theoretically dynamic structures in which the component lipids and proteins can move about and undulate relatively freely. Nevertheless, the exchange of individual molecules with the surrounding solution will be significantly slower than in micelles, so that the structure as a whole remains intact. It simply would not do to have biological cells falling apart too often. To carry out its biological function, the cell membrane will also have heterogeneous regions of lipids, proteins, or other materials, which may serve as specific binding sites, transport “channels,” etc. The components of the entire structure, however, must all have one thing in common: they must be able to associate spontaneously to form the necessary stable assembly of molecules to do the job, even when some of the components (e.g. cholesterol and lipids) will not form suitable structures alone. It appears that an organism can “sense” the specific lipid structures needed in a given situation to produce the required membrane structure with the necessary fluidity, surface characteristics, ionic sensibilities, etc. to carry out its function.

When conditions such as temperature change, the organism often synthesizes new molecules (more or less saturated fatty acid chains in a lipid, for example) to fit the new conditions. Clearly, the creation and functioning of biological membranes cannot be a haphazard process of trial and error in selecting the proper lipids for a given cell structure. There must be some feedback mechanism through which the organism “knows” what material characteristics are needed under a given set of conditions so that it can be provided when and where called for. In Chapter 14 less common surfactant structures termed gemini and bolaform surfactants will be discussed. Those surfactants, often isolated from microorganisms, clearly show the extremes that biological systems can go to protect their integrity in the face of extreme environmental conditions.

Other aspects of the interactions of lipids and bilayer structures in biological systems can be understood in the context of molecular geometry, association phenomena, and general interfacial interactions. Unfortunately, those topics are too broad to be included here. It will be interesting to see how future research in molecular biology is able to incorporate the fundamentals of surface and colloid science into a better understanding of the function of membranes, cells, and entire organisms.

7.7 Microemulsions

As indicated above, the status of systems commonly called microemulsions among surface and colloid chemists is somewhat uncertain, despite very extensive investigations and discussions in recent years. Various experimental approaches have been used in an attempt to ascertain all the details of their thermodynamic and structural characteristics. As a result, new theories of the formation and stability of these interesting but quite complex systems are appearing. Hand in hand with understanding have come ideas for new potentially useful applications. Although a great deal is known about microemulsions, there is much more to be learned about the requirements for their preparation and the relationships among the chemical structure of the oil phase, the composition of the aqueous phase, and the structures of the surfactant and the co-surfactant, where needed. As new data become available, it is clear that any discussion of structure–property relationships between surfactants and microemulsions becomes just as rapidly outdated. There are several excellent books and reviews that address the theoretical and practical aspects of microemulsion theory

and practice cited in the Bibliography. The following discussion is limited to the presentation of comparisons among microemulsions and related systems (swollen micelles and macroemulsions, for example) and some general relationships that have been developed between surfactant structures and microemulsion formation.

The distinction between microemulsions and conventional emulsions is fairly clear. Although emulsions may be kinetically stable for long periods of time, they must all, in the end, suffer the same fate – phase separation to attain a minimum in interfacial free energy. The actions of surfactants, polymers, and other stabilizing aids may shift the rate of droplet coalescence to extremely long times through decreased kinetic rate constants, but the thermodynamic driving force to minimize interfacial area of contact between immiscible phases remains unchanged. Microemulsions, on the other hand, appear to be thermodynamically stable compositions with essentially infinite lifetimes, assuming no change in such factors as composition, temperature, and pressure.

In addition to the thermodynamic distinction usually drawn between macro- and microemulsions, the two classes of colloids differ in several other more tangible characteristics, including the size of droplets formed and the mechanical requirements for their preparation. As far as droplet size is concerned, emulsions generally have relatively large particle diameters, meaning that such systems are usually quite turbid or opaque. Microemulsions, however, normally have droplet diameters of 100 nm or less, with many being only slightly larger than micellar systems. Because those particles are much smaller than the wavelength of visible light, they are normally transparent or slightly bluish.

The energy requirements for the formation of emulsions can be quite substantial. The formation of small droplets requires that the system overcome both the adverse positive interfacial free energy between the two immiscible phases working toward drop coalescence and bulk properties of the dispersed phase such as viscosity. Microemulsions, on the other hand, form spontaneously with little or no agitation required when the proper composition of the system is reached.

When one compares microemulsions and micelles, the demarcation line can become quite blurred and, in some cases, does not exist. As noted earlier, there is some controversy as to the true definition of clear, isotropic solutions of oil, water, and surfactant (and co-surfactant, if needed) as microemulsions rather than swollen micelles. Although the differences between the two systems may appear to be more semantic than physical, several arguments can be put forward that strongly support a differentiation of the two systems. Although there is no need to overemphasize the philosophical aspects of the subject, a synopsis of the current situation may be useful in helping to understand the impact of the molecular structures of the components on the characteristics of the final system.

If one constructs a “spectrum” of the possible situations for the dispersion of one liquid phase in another, oil in water, for instance, the possible sizes of the dispersed phase units range from the molecularly dispersed solution where “droplet” sizes are on the order of a few nanometers to emulsions with droplet diameters of hundreds or thousands of nanometers (Figure 7.9). Lying between the extremes are micelles (a few tens of nanometers), macromolecular solutions (tens to hundreds of nanometers), and colloids of several hundred to several thousand nanometers. The systems typically referred to as microemulsions will normally have particle sizes between 5 and 200 nm, generally well beyond the range of normal micelles in dilute solution. Classifications such as those illustrated in Figure 7.9 are certainly arbitrary in their ranges, and some overlap inevitably occurs; however, the physical differences encountered among most of the different groups are sufficient to obviate any controversy as to their general definitions.

The problem of the thermodynamic differentiation between micelles and microemulsions is less amenable to easy solution. While it is undoubtedly true that, in the smaller size ranges especially,

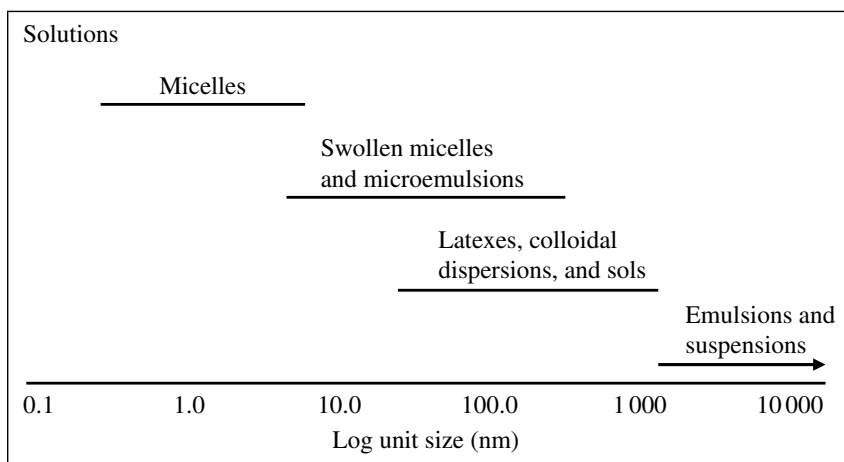


Figure 7.9 A “spectrum” of approximate size ranges for surfactant aggregates and dispersions.

many systems classed as microemulsions are almost indistinguishable from swollen micelles, it is equally true that the larger microemulsion systems far exceed the solubilizing capacity of micelles. Micelles will form under many circumstances, although the specifics of **cmc**, aggregation number, etc. may change with the environmental conditions. The formation of microemulsions, on the other hand, has been shown to have very specific compositional requirements. It is primarily because of those specific demands on the composition of the system and the chemical structures of the various components that the nomenclature for this separate class of dispersed species has developed.

In the literature on the solubilization of hydrocarbons, dyes, etc. in micellar solutions, the ratio of solubilized molecules to surfactant molecules very rarely exceeds, or even approaches, two. Many microemulsion systems, on the other hand, have been described in which the ratio of dispersed phase to surfactant (and co-surfactant) exceeds 100. Because of the relatively low ratios of additive to surfactant obtainable in micellar systems, it is clear that there can exist no oil phase that can be considered separate from the body of the micelle. That is, the solubilized oil phase is present as individual molecules intimately associated with the micelle structure. In many microemulsions, however, the size of the droplet and the high additive-to-surfactant ratio require that there be a core of dispersed material that will be essentially equivalent to a bulk phase of the additive. The seemingly obvious conclusion is that the microemulsion systems possess an interfacial region composed primarily of surfactant and co-surfactant, analogous to that encountered in emulsions, but with the difference that the interfacial region is thermodynamically stable.

Extensive work on microemulsions has led to the postulation that the driving force for the spontaneous formation of such dispersed systems is the existence of a transiently negative interfacial tension between the oil and water phases, resulting in a rapid transfer of one of the two phases through the interface, producing the optimum droplet size for the given composition. It must be emphasized that the negative interfacial tension is a transient phenomenon and at equilibrium must be zero or slightly positive.

As mentioned above, the spontaneous dispersion of one liquid phase in another can occur only if the interfacial tension between the two phases is so low that entropy effects due to the dispersion process can dominate the total energy of the system. Although many surfactants can lower the interfacial tension between oils and water substantially, such factors as micelle formation,

solubility limits, and interfacial saturation normally prevent the attainment of the required low values for microemulsion formation. For ionic surfactants in particular, the nature of the head group will usually lead to the formation of rather rigid interfacial films, which limit surfactant mobility in the film and the curvature that may be obtained in the interfacial region. The addition of a co-surfactant, usually an alcohol or amine of short- or medium-chain length, can serve to reduce the rigidity of the interfacial film and increase adsorption at the interface.

According to the Gibbs equation, the surface or interfacial tension of a system, σ , is related (approximately) to the amounts of surface-active materials preferentially adsorbed at the interface by

$$d\sigma = -\Gamma_i RT d(\ln C_i) \quad (7.2)$$

where Γ_i is the surface excess of component i at the interface and C_i is its concentration in the bulk solution. From the equation it is clear that the positive adsorption of any material at the interface will result in a lowering of the interfacial tension. The maximum value of Γ_i attainable for a single-component surfactant system is usually limited by solubility, **cmc**, or geometric restrictions, so very few such systems can produce the low values of σ required for spontaneous dispersion. Some notable exceptions to that rule are sodium di-2-ethylhexyl-sulfosuccinate and some POE nonionic surfactants at temperatures near their cloud point.

If increased adsorption at the interface is needed, then the addition of a material that can circumvent or overcome the negative aspects of the single-component surfactant system may achieve the desired result. From Chapter 6 it can be recalled that the addition of many alcohols of short- to medium-chain length, the already referred to co-surfactants, will increase the **cmc** of ionic surfactants and increase their solubility in the aqueous phase. Both effects work in favor of microemulsion formation as postulated above, especially from the standpoint of the solution properties of the surfactant.

If, in addition to improving the solution properties of the surfactant, the added alcohol can be preferentially adsorbed at the oil–water interface, the third barrier preventing the attainment of very low interfacial tensions can be attacked. Because of the relatively large differences in size between the surfactant and co-surfactant, the alcohol molecules, having a cross-sectional area of only a few square angstroms, can efficiently pack themselves between the larger surfactant chains at the interface. The smaller size and lower hydrophilicity of the hydroxyl group can also moderate the electrostatic and steric interactions among the primary surfactant head groups. The net result is a more densely packed interfacial layer (a much larger positive value of Γ_i), which makes possible very low and transiently negative interfacial tensions. In addition, the mobility of the interfacial layer is increased by the plasticizing (by analogy to polymeric systems) effect of the smaller co-surfactant molecules. The situation is pictured schematically in Figure 7.10.

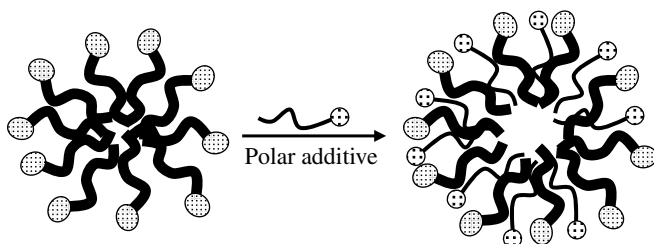


Figure 7.10 Schematic representation of the enhanced packing efficiency of surfactants in the presence of polar additives.

It should be pointed out that although the preceding discussion was concerned with the use of alcohols as co-surfactants in microemulsion formation, many other types of material can also be used to the same end. Especially important are primary amines (commonly used with cationic surfactants) and thiols.

7.7.1 Surfactants, Co-surfactants, and Microemulsion Formation

Microemulsions are composed of two mutually immiscible liquid phases, one spontaneously dispersed in the other with the assistance of one or more surfactants and co-surfactants. While microemulsions of two nonaqueous liquids are theoretically possible, fluorocarbon/hydrocarbon systems, for example, almost all the reported work is concerned with at least one aqueous phase. The systems may be water continuous (O/W) or oil continuous (W/O), as illustrated in Figure 7.11, the result being determined by variables such as the surfactant/co-surfactant system employed, temperature, electrolyte levels, the chemical nature of the oil phase, and the relative ratios of the components.

From the figure, it is clear that in O/W microemulsions the surfactant tails are most constrained or crowded, while in the W/O case it is the head group that is space limited. In the case of ionic surfactants, the head group crowding will obviously introduce significant electrostatic repulsion among the charges and significantly affect the character of the monolayer. The crowding of the surfactant tails in the O/W case is much less of a problem since such crowding is actually favored, up to a point, by attractive hydrophobic interactions. Such qualitative evaluations have been found to be useful for predicting the “sense” of microemulsions formed, especially for borderline compositions. The use of three- and four-component phase diagrams makes it possible to determine the relationships among the various components with a fair degree of precision and thereby predict the character of the microemulsion to be expected for a given composition.

The character of a microemulsion, or whether one will be formed at all, is critically dependent on the structures of the surfactants and co-surfactants employed and the relative quantities of each in the system. As mentioned above, most microemulsions, especially those employing an ionic surfactant, will require the addition of a co-surfactant to attain the required interfacial properties to allow for the spontaneous dispersion of one phase in the other. Nonionic surfactants, on the other hand, quite often form microemulsions without the addition of another component.

7.7.1.1 Ionic Surfactant Systems

Using the schematic picture presented in Figure 7.11, it is possible to qualitatively analyze the relationship between surfactant and co-surfactant structures and the most probable microemulsion system formed for ionic surfactants. If the ratio of co-surfactant/surfactant is less than three, the surfactant head groups can approximate a close-packed monolayer for Type 1 curvature, and the formation of a O/W system is favored. If the ratio is three or greater, close packing of the head groups is not possible, and W/O systems are predicted. Longer-chain cosolvents will tend to favor W/O systems, all things being equal, while electrical double-layer effects will tend to push for O/W systems.

Although the thermodynamic theory of microemulsions still has some way to go to be more or less complete, a number of generalizations can be made regarding ionic surfactant microemulsions.

- 1) A co-surfactant is always required to form W/O microemulsions using ionic surfactants, not only to lower the interfacial tension, σ , but also to reduce head group crowding due to the Type 2 curvature.

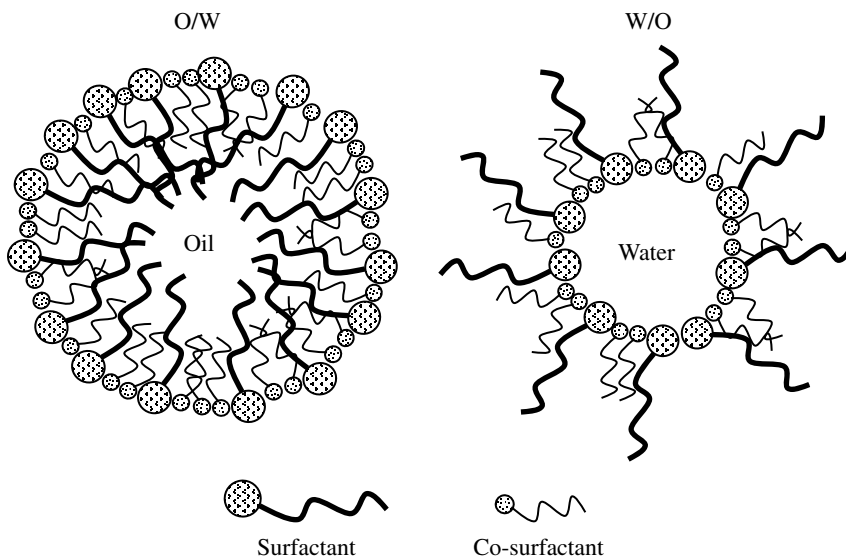


Figure 7.11 A schematic representation of O/W and W/O microemulsions including co-surfactants.

- 2) O/W microemulsions require less co-surfactant than W/O systems, all other things being equal (OTBE).
- 3) Electrical double-layer effects favor O/W systems. As a result, the addition of electrolyte will tend to push the same surfactant/co-surfactant system toward the formation of W/O microemulsions.
- 4) Increasing the chain length of the cosolvent will tend to move the same surfactant system toward the formation of W/O microemulsions (OTBE).

7.7.1.2 Nonionic Surfactant Systems

Many nonionic surfactants such as the alkylphenol-POE ethers form microemulsions. When compared with systems involving ionic surfactants, a number of important differences are evident:

- 1) In most case, no co-surfactant is needed, even for pure surfactant samples in which the POE chain has been purified, rather than the normal distribution of chain lengths found in commercial materials.
- 2) Because of the temperature–solubility relationship for POE nonionic materials, the system temperature becomes an important variable in determining the character of the final microemulsion.
- 3) Not surprisingly, nonionic microemulsion systems are much less sensitive to electrolytes than ionic systems, although any effect will be in the same sense as that for ionic systems.
- 4) For alkylphenol-POE nonionic surfactants of a constant HLB but different alkyl and POE substitutions, an increase in surfactant molecular weight (tail + head group) results in an increase in the amount of oil that can be included in the system before a second phase begins to form. Branching of the hydrocarbon tail, on the other hand, results in a decrease in oil incorporation capacity.

When the length of the POE chain is increased for a given tail, the optimum temperature for solubilization of an oil in aqueous micellar solution is shifted upward. If the temperature of the

system for a given POE chain is increased, the hydration of the POE chain by water will decrease, leading in many cases to an inversion in microemulsion type from O/W to W/O.

7.7.2 Applications

The spontaneous formation of microemulsions, their almost monodisperse particle size, and their thermodynamic stability make them very attractive for applications that involve oil–water mixtures. In many cases, almost transparent systems also provide a degree of esthetic appeal.

The most important applications of microemulsions to date are probably found in cosmetics and tertiary oil recovery, where esthetic factors and the attainment of very low interfacial tensions are of prime importance. In the petroleum industry, microemulsions theoretically would allow the difficult to recover residual oil to be pushed efficiently through the rock formation without being retarded by the development of a large pressure drop across the highly curved membranes as given by the Laplace equation

$$\Delta p = 2\sigma/r \quad (7.3)$$

Equation (7.3) states that the pressure differential or drop across a curved interface will be directly proportional to the interfacial tension, σ , and inversely proportional to the radius of curvature, r . As the drop size decreases, Δp increases for a given value of σ . Lowering the value of σ helps to overcome the increased pressure differential and facilitate the movement of the oil. Although the use of microemulsions in tertiary oil recovery has shown great promise for a number of years, the special conditions of temperature, salinity, and other factors that impact on microemulsion formation and stability place a number of roadblocks in the road to their widespread application.

Other application or potential application areas include cutting oils and special lubricating systems, dry-cleaning systems, self-emulsifying oils for plant protection, floor and furniture polishes, leather treatments, cosmetics, and pharmaceuticals.

8

Surfactant Self-Assembled Aggregates at Work

In addition to being one of the fundamental thermodynamic consequences of the nature of amphiphilic molecules, micelles and other higher aggregate structures produced in surfactant solutions have a significant practical impact on the application of surfactants in various technological areas. The technologically important phenomena related to micellar solubilization and micellar catalysis deserve special mention in any discussion of surfactant technology, especially in view of the increasing attention they are receiving in both academic and industrial circles. The ability to incorporate inherently insoluble (or only slightly soluble) materials into a solvent system in a stable, reproducible, and readily characterized way has many significant technological implications and applications. Two examples having potentially great economic and social importance include new drug delivery systems and tertiary oil recovery methods. Other areas of application in personal care products, agriculture, medicine, foods, biotechnology, etc. can be conceived of by the innovative scientist.

This chapter focuses on three types of phenomenon that are closely related to the presence of amphiphiles and micelles in solution and on the roles surfactant structures and other characteristics may play in their application. To exploit the micellar nature of surfactants and to realize their technological potential, it is necessary for the investigator to understand and very carefully control the many variables involved in the various phenomena. It is probable that the next few years will see a dramatic increase in the use of micellar and related systems to produce better, more effective, more appealing, and (hopefully) cheaper products for the realization of a better world.

From the dawn of science and the “sometimes-science” of the alchemists, a major goal has been the emulation of natural processes in bringing about chemical change, in addition to the “classical” desire to change base metals into gold. The quiet prayer of many synthetic chemists has long been that their reaction pathways would someday approach those of nature’s enzymes in speed, efficiency, and effectiveness. While modern chemical techniques have made it possible to prepare many unique compounds that do not seem to appear in nature (probably because there is no “natural” need for them), those preparations usually involve such extreme measures or produce such low yields that they are in fact little more than scientific curiosities, even if they do add greatly to our basic knowledge of the world about us. On the other hand, a number of natural compounds that can be of great benefit to mankind can be obtained synthetically or from biological sources in small quantities and at great expense. We seem to have difficulty reproducing many of the actions of nature’s workmen the enzymes. In the past few decades, the application of the principles of surface activity and surfactants has allowed science to begin to understand and replicate (roughly) enzymatic processes. The new age of transgenic microbial, plant, or animal production of desired

natural products is, of course, one route for circumventing nature. The technological and sociological impact of that new technology remains in question, however.

The following discussions are only brief surveys of some of the subjects involved and barely begin to address the large amount of theoretical and experimental information available. They are intended to introduce some of the basic concepts involved in each case so that readers can more readily formulate ideas as to the potential applicability of such phenomena to their own needs. The information presented should serve at least as a good starting point for pursuing those ideas.

8.1 Solubilization in Surfactants Micelles

The increased solubility of organic materials in aqueous surfactant solutions is a phenomenon that has found application in many scientific and technological areas. It is only recently that a good understanding of the structural requirements for optimum solubilization has begun to develop as a result of extensive experimental and theoretical work. Empiricism is slowly giving way to well-thought-out correlations between the requirements of a system and the chemical structure of surfactant that will provide the necessary environment to promote the solubilization process.

Early work in the twentieth century addressing the mechanisms of micellar solubilization was, unfortunately, often performed with surfactants of questionable purity. As described in Chapter 6, small quantities of impurities and isomeric variations in the structure of the surfactant can have a significant impact on the micellization process and, naturally, on solubilization phenomena related to it. More recently, closer attention has been paid to using the purest or best characterized surfactant systems available so that more confidence can be placed in the validity and interpretation of experimental results. That is not to say, however, that the pioneering work of the first half of the last century was without merit. To the contrary, modern experimental techniques have done much to confirm the work of that era. Considering the relatively limited resources of the early investigators (compared to the modern chemical laboratory), one can only regard their results and interpretations with the highest respect.

When discussing a subject such as micellar solubilization, it is very important to define exactly what is meant by the term. As is often the case, there is some disagreement within the surfactant literature as to the fine points of the definition of solubilization, particularly as the ratio of surfactant to additive decreases and one approaches the nebulous frontier between swollen micellar systems and the microemulsions discussed in Chapter 7 and emulsion regimes to be discussed in Chapter 10. For now, the discussion is limited to systems in which the micelle is clearly the primary vehicle for the observed phenomenon.

For present purposes, solubilization is defined as a spontaneous process leading to a thermodynamically stable, isotropic solution of a substance (the additive) normally insoluble or only slightly soluble in a given solvent produced by the addition of one or more amphiphilic compounds, including polymers and hydrotropes, at or above their critical micelle concentration (**cmc**). By the use of such a definition, a broad area can be covered that includes both dilute and concentrated surfactant solutions, aqueous and nonaqueous solvents, all classes of surfactants and additives, and the effects of complex interactions such as mixed micelle formation. It does not, however, limit the phenomenon to any single mechanism of action.

The history of solubilization research in the first half of this century has been extensively reviewed, and several pertinent references are given in the Bibliography. Although there are many aspects to understanding solubilization phenomena, this discussion is primarily concerned with the correlations that can be made between the molecular structure of a surfactant and its activity

and capacity as a solubilizing agent, the related effects of the chemical nature of the additive, and the role of the solution environment. For a specified solvent system, water or aqueous solutions, for example, two variables must be considered in the solubilization process: (i) the molecular nature, purity, and homogeneity of the surfactant and (ii) the chemical nature of the additive. From a technological viewpoint, it is important to understand exactly what surfactant structural features serve to maximize the desired solubilizing effect, and the best way to achieve that understanding is through a fundamental knowledge of the molecular and thermodynamic processes involved. In addition, since most technological applications of solubilization (detergent action, for instance) involve complex multicomponent systems, such factors as temperature, electrolyte content, and the presence of polymeric species and other solutes must be examined. Obviously, for such applications as cleaning and detergency, it is not possible to completely specify the system with anticipation; therefore, consideration must always be given to attaining broad solubilizing capabilities, often at the expense of the optimum for a specific “model” set of circumstances.

Before addressing some of the specific aspects of the influence of surfactant structure on solubilization, it will be useful to understand the “geography” of solubilization – that is, the possible positions in (or on) the micelle that can serve as host sites for the additive molecules and the factors that determine exactly where solubilization will occur.

8.1.1 The “Geography” of Solubilization in Micelles

It is well established that the location of a solubilized molecule in a micelle relative to the structural components of the surfactant will be determined primarily by the chemical structure of the additive (Figure 8.1). In aqueous solutions, nonpolar additives such as hydrocarbons are intimately associated with the core of the micelle (Figure 8.1a), while slightly polar materials such as long-chain fatty acids and alcohols, esters, amides, nitriles, and the like are usually located in what is termed the palisades layer (Figure 8.1b) lying near the transition zone between the hydrophobic micellar core and the more hydrophilic outer layer of the aqueous micelle. The orientation of such molecules is probably more or less radial, with the hydrocarbon tail remaining closely associated with the micellar core. In some cases, that orientation can potentially have a significant effect on the nature of the system, as discussed in the Section 7.7. Other structural factors, such as the charge on the surfactant head group, can significantly affect the locus of solubilization. Materials containing aromatic rings, for example, may be solubilized in or near the core of anionic systems, but in the palisades layer of cationic micelles because of polarization interactions between the aromatic ring and the cationic head group.

In addition to the solubilization of additives in the micellar core and the core–palisades boundary region, they may also be found entirely in the palisades region (Figure 8.1c) and on the micellar surface (Figure 8.1d). The nature of the polar head group of nonionic surfactants, especially the polyoxyethylene derivatives, is such that a relatively large fraction of the micelle volume corresponds to the palisades region. Because of the bulky nature of the POE chain and its attendant solvent molecules, it has been suggested that the hydrophilic chain is arranged in an approximate spiral from the micellar core outward into the solution. As a result, areas of the palisades near the core will be sterically crowded with the POE chains, with relatively little room left for waters of hydration or casual water molecules. As the distance from the core increases, the palisades layer becomes more hydrophilic, acquiring more characteristics of an aqueous solution. The net effect of such a situation is that, deep in the palisades layer, the chemical environment may resemble that of a polyether so that materials soluble in such solvents will be preferentially located in that region.

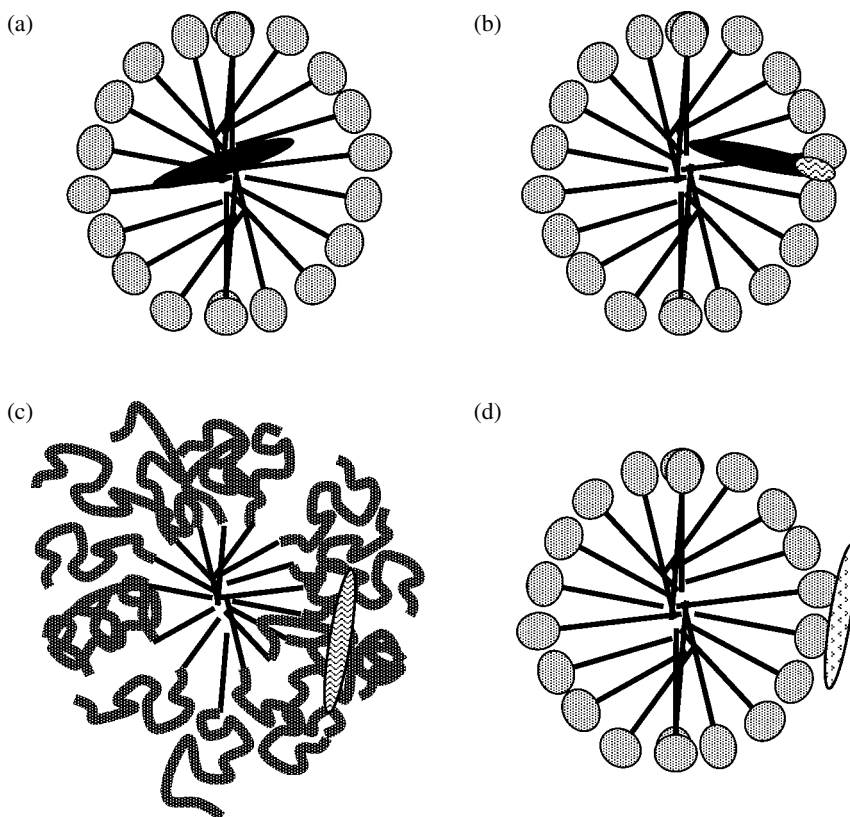


Figure 8.1 Loci for the solubilization of additives in micelles (a) micelle core (b) core/palisades interface (c) surface region (nonionics), and (d) on micelle surface (ionics).

Even though chemical structures may dictate the preferred location for the additive, solubilized systems are dynamic, as are the parent micelles, and the location of specific molecules may change over time. It will always be important to remember, then, that while a given region of the micelle may be preferred by an additive on chemical grounds, there is no guarantee that all phenomena related to the system (catalysis, for example) will be associated with that region.

In surfactant/nonpolar solvent systems where the orientation of the micelle is reversed, the polar interactions of the head groups not only provide a driving force for the aggregation process, but they also provide an opportune location for the solubilization of polar additives. Water is, of course, one of the most important potential polar additives to nonaqueous systems, and it is primarily located in the polar core. The nature of such solubilized water is not fixed, however. It has been shown, for example, that in the system benzene/(sodium di-2-ethylhexylsulfosuccinate)/water, the initial water added is tightly associated with the ionic head group of the surfactant (as waters of hydration), while subsequent additions appear to have the character of free bulk water. Other polar additives such as carboxylic acids, which may have some solubility in the organic phase, are probably associated with the micelle in a manner analogous to that for similar materials in aqueous systems.

The effects of solubilized additives on the micellar properties of nonaqueous surfactant systems vary according to the structures of the components. Since such changes are often greater than those found in aqueous solutions, however, care must be exercised in evaluating the effects of even

small additions on the aggregation characteristics of surfactants in nonaqueous solvents. Because of the industrial importance of nonaqueous surfactant systems as cutting oils, lubricants, and corrosion inhibitors, a great deal of knowledge about such systems is closely held by the various industrial and governmental organizations involved in the related research. As a result, there are a number of gaps in our understanding of the structural relationships among surfactant, solvent, and additive. If more readily available, such information might facilitate the extension of current knowledge to new applications.

8.1.2 Surfactant Structure and the Solubilization Process

Earlier chapters introduced some of the wide array of chemical species that exhibit surfactant properties and are potentially useful in solubilization processes. Just as molecular structure is important to such surfactant characteristics as the **cmc**, aggregation number, and micellar shape, it also controls the ability of a surfactant to solubilize a third component. Conversely, the presence of a third component in a surfactant solution can often affect its aggregation characteristics. It is documented in a number of reports that the presence of a solubilized additive, even though the additive has no inherent surface activity, can change the **cmc** of a surfactant substantially from that of the pure system. As noted in Chapter 6, the existence of such an effect means that great care must be exercised in the interpretation of experimental data on micellization derived from solubilization results.

Whether micelles formed in the presence of a third component are the same as those formed in its absence is a subject of some controversy. It has been shown that micellar activity may be induced in surfactant solutions below the “normal” **cmc** in the presence of small amounts of solubilized additives. In some cases, such effects have been attributed to additive-induced micellization. In others, effects have been seen at concentrations several orders of magnitude below the **cmc**, suggesting the presence in solution of sub-micellar species possessing some properties of the fully aggregated system.

Some researchers have suggested that surfactants in dilute solution undergo a low level of molecular aggregation at concentrations well below their **cmc**, during which dimers, tetramers, and other “pre-micellar” aggregates are formed. That may be especially true for surfactants having unusually large or bulky hydrophobic groups, such as the bile acids and tetraalkylammonium halides. Large reaction rate enhancements have been found for such materials when used as phase transfer catalysts (see below), suggesting that they are acting in a micelle-like fashion even though normal micelle formation is precluded by their molecular structure. Some effect due to the formation of tight or solvent-separated ion pair aggregates is usually invoked to explain the observed catalytic results.

Since the **cmc**'s of most surfactants occur at rather low concentrations, evidence of pre-micellar aggregate formation quite often becomes a question of the interpretation of results lying at the limits of sensitivity and accuracy of many experimental techniques, and, of course, the view of the individual interpreter of those results. There seems to be little doubt that in nonaqueous solvents, the formation of dimer and other lower aggregates occurs readily. Fluorescence and electron spin resonance techniques have also shown the presence of such species in very bulky surfactant systems in water. However, there is presently little unambiguous evidence to confirm the occurrence of pre-micellar aggregation as a general rule in conventional aqueous surfactant solutions.

The discussions of micelle formation given in Chapter 6 indicated that surfactant properties such as the **cmc** and aggregation number can be reasonably well correlated with the size and nature of the hydrophobic group. In each case, as the hydrophobic group increases in size for a

given head group, the **cmc** decreases, and the aggregation number increases within a homologous series. No comparable relationships have so far been determined that can accurately relate surfactant structure and solubilizing power, mainly because the structure of the additive can play such an important role in the overall aggregation process.

As already mentioned, hydrocarbons and polar organic compounds with low water solubility are usually found to be solubilized in the interior of the micelle or deep in the palisades layer. It has generally been shown that, not surprisingly, the amount of such materials solubilized increases as the size of the micelle increases. As a result, any of the factors discussed in Chapter 6 that cause an increase in micelle size might also be expected to increase the solubilizing power of the system. An increase in the length of the hydrocarbon chain, for example, leads to a lower **cmc** and larger aggregation number so that more of a nonpolar additive can be incorporated into the micellar core per mole of surfactant in the system (Table 8.1).

In a study of the solubilization of ethylbenzene in a series of potassium carboxylates ranging from C_8 to C_{16} , it was found that as the concentration of surfactant increased, the amount of ethylbenzene solubilized increased and that as the length of the carbon chain increased, the quantity of material incorporated per mole of surfactant increased with the carbon chain length. Such results have been criticized because of the assumption that the activity of the monomeric surfactant remained constant above the **cmc** so that the amount of surfactant in the micelles could be quantified by subtracting the **cmc** from the total amount present. It is now known that such an assumption is not strictly valid. Substantially the same results have been found in other studies with different surfactants and additives, however. It was found, for example, that the amount of dimethylaminoazobenzene incorporated by a series of potassium carboxylate soaps appeared to be almost linearly related to the carbon number of the surfactant.

Branching of the hydrocarbon chain of the surfactant usually results in a decrease in the solubilizing power of the system relative to that of the analogous straight-chain material. That is presumably due to geometric and packing constraints, which limit the ability of the micellar core to

Table 8.1 The effect of surfactant hydrocarbon chain length on **cmc** and the solubilization of ethylbenzene in potassium soap solutions.

Surfactant (M)		cmc (M)	Solubilized
$C_7H_{15}COO^-$	(0.48)	0.66	0.141
	(0.83)		0.152
$C_9H_{19}COO^-$	(0.44)	0.17	0.197
	(0.72)		0.233
$C_{11}H_{23}COO^-$	(0.20)	0.046	0.364
	(0.50)		0.407
	(0.86)		0.522
$C_{13}H_{27}COO^-$	(0.24)	0.012	0.745
	(0.50)		0.866
	(0.57)		0.888
$C_{15}H_{31}COO^-$	(0.15)	0.0032	1.15
	(0.29)		1.48

Moles solubilized per mole of soap in micelles.

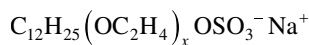
accommodate the added bulk of the solubilized molecules. The addition of ethylenic unsaturation and aromatic groups also tends to decrease the maximum amount of additive that can be fitted into the core packing arrangement.

In the case of nonionic surfactants, the amount of aliphatic hydrocarbon that can be solubilized generally increases as the length of the hydrophobic tail increases and decreases as that of the POE chain increases. Those results parallel changes in the **cmc**'s and aggregation numbers of the respective materials. Divalent salts of alkyl sulfates quite often exhibit a greater solubilizing capacity than the corresponding monovalent salts for materials included in the micellar core. That result has been related to the increase in volume of the micellar core of the divalent salts.

The relative solubilizing power of the different types of surfactant with a given hydrophobic tail usually follows the order nonionics > cationics > anionic. The rationale for such a result is usually related to the supposed looser packing of the surfactant molecules in the micelles of the nonionic materials, making available more space for the incorporation of additive molecules.

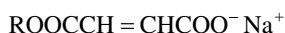
If one considers additives with a more polar character, which might reasonably reside in or near the palisades layer, fewer generalizations like those above can be made. The complex interactions among the various components of the system – the surfactant head groups, water (or other solvent) molecules, the exposed micellar core, and the polar group of the additive – appear to be too specifically sensitive to allow for an easy trend analysis.

It is usually found that compounds such as methyl isobutyl ether and *n*-octyl alcohol were better solubilized in 0.1 N sodium oleate than in potassium laurate at the same concentration and temperature, contrary to the results for hydrocarbon materials solubilized in the micellar core of the same systems. Octylamine, on the other hand, was incorporated into each to an equal extent. It is also found that the degree of solubilization of 1-*o*-tolyl-azo-2-naphthylamine and related materials in micelles of sodium dodecyl polyoxyethylene sulfates,

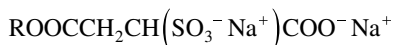


where *x* varied from 1 to 10, increases as the value of *x* increased. The same material showed no change in solubilization with increase in the POE chain length in the analogous un-sulfated non-ionic surfactant over the range of *x* = 6–20. That result was attributed to the compensating effects of an increased potential for solubilization due to the increase in the POE chain and a decrease due to a smaller aggregation number. The solubilization of Yellow OB dye in both the sulfated and un-sulfated POE surfactants was greater than that in the corresponding sodium alkyl sulfate.

The addition of a second polar group to a surfactant molecule can either increase or decrease its solubilizing power, depending on the nature of the additive. Studies comparing the solubilizing capacity of the monoesters of maleic acid



with those of the disodium salts of the equivalent monoesters of sulfosuccinic acid



found that the introduction of the second ionic group decreased the solubilizing capacity for nonpolar additives such as *n*-octane, while that for *n*-octanol was increased. Based on the preceding discussion, that result can be explained by the fact that the introduction of the sulfonate group decreases the aggregation number of the micelle, thus limiting its capacity to include the

hydrocarbon in the core. At the same time, the bulky ionic groups increased the steric requirements at the micelle surface, increasing the relative volume of the palisades layer available to the more polar *n*-octanol molecules.

The solubilizing power of amphoteric surfactants has not been as widely studied, or at least as widely reported, as that for the simpler ionic and nonionic materials. However, the available data indicate a solubilizing capacity range somewhere between the extremes, the exact results possibly being more sensitive to the nature of the additive than those for the other classes of surfactants.

8.1.3 Solubilization and the Nature of the Additive

The quantity of a substance that can be solubilized in surfactant micelles will depend on many factors, some of which have already been discussed. From the standpoint of the additive itself, such factors as molecular size and shape, polarity, branching, and the electronegativity of constituent atoms have all been found to be of some significance, depending on the exact system. One of the most extensively explored factors relating the chemical structure of the additive to its solubilization has centered around the relationship between the molar volume of the additive and the maximum amount of material that can be incorporated in a given surfactant solution. Investigations into the solubilization of the hydrocarbons hexane, heptane, and octane, and the aromatics benzene, toluene, ethylbenzene, propylbenzene, and butylbenzene, showed that there existed an inverse relationship between the molecular volume of the additive and the amount of material solubilized. A similar study of polycyclic aromatics in sodium laurate gave similar results. In each study, linear relationships between the logarithm of the volume of the material solubilized and its molar volume were obtained, although the slopes of the plots differed for the different classes of compounds studied.

In general, the chemical nature of the additive can be classified as either nonpolar, such as simple hydrocarbons, or polar, such as the long-chain alcohols, esters, amides, and nitriles. As is usually found when discussing surfactants, however, such simple classifications are never so nicely clear-cut in reality. In the same way that the hydrophobic character of a surfactant can be varied almost continuously over a wide range, the polar character of a potential additive can be made to span a rather broad spectrum. The aromatic unsaturation of the benzene ring, for example, is sufficiently polarizable that its presence can cause a material to perform like a polar additive, even in the absence of any truly polar functionality, especially in conjunction with cationic surfactant systems.

There does not seem to be a single, simple relationship that correlates a property of a potential additive with its tendency for solubilization in a given surfactant system. Generalizations based on chemical structures are limited and vary a great deal with the characteristics of the complete system – solvent, surfactant, and additive. Examples of such varied results can be seen in Tables 8.2 and 8.3, which list the maximum additive concentrations (MAC) achieved under given conditions of surfactant concentration and temperature. For the case of nonionic surfactants (Table 8.2), it can be seen that as the polarity of the additive increases, the ability of the micelle to accommodate the material increases. Such a result is indicative of solubilization occurring in the palisades layer of the micelle. From the results in Table 8.3, in which various surfactant types can be compared, it is clear that for nonpolar additives, the cationic surfactants are superior solubilizing agents to the two anionic materials tried, with the unsaturated oleate being better than the related saturated compound on a mole-for-mole basis. For the polarizable aromatic additives, the cationic surfactants lose their advantage, indicating that such materials are prone to polarization by the cation, which results in solubilization outside the core in the palisades region. With truly polar additives,

Table 8.2 Maximum additive concentrations (MAC) solubilized in 1% aqueous solutions of $C_{10}H_{21}(OE)_{10}CH_3$ nonionic surfactant at 27°.

Additive	MAC		
	g/L	mM/L	Mol/mol of surfactant
<i>n</i> -Octane	0.9	7.9	0.48
<i>n</i> -Decane	0.39	2.7	0.17
<i>n</i> -Dodecane	0.16	0.9	0.06
<i>n</i> -Decylchloride	0.45	2.6	0.16
<i>n</i> -Octanol	3.12	24.0	1.47
<i>n</i> -Decanol	2.38	15.1	0.93
<i>n</i> -Dodecanol	2.07	11.1	0.68
<i>n</i> -Decylamine	3.78	24.1	1.48
<i>n</i> -Decanoic acid	2.30	13.4	0.82

Table 8.3 MAC solubilized by typical ionic surfactants compared with a C_{10} nonionic.

Additive	MAC (mol/mol surfactant)			
	$C_{12}NH_3^+ Cl^-$	$C_{12}COO^- Na^+$	$C_{18}COO^- Na^+$	$C_{10}(OE)_{10}CH_3$
<i>n</i> -Hexane	0.75	0.18	0.46	—
<i>n</i> -Heptane	0.54	0.12	0.34	—
<i>n</i> -Octane	0.29	0.08	0.18	0.48
<i>n</i> -Decane	0.13	0.03	0.05	0.17
<i>n</i> -Dodecane	0.06	0.005	0.009	0.06
Cyclohexane	0.87	0.23	0.56	—
Benzene	0.65	0.29	0.76	—
Toluene	0.49	0.13	0.51	—
Ethylbenzene	0.38	0.20	0.40	—
<i>n</i> -Octanol	0.18	0.29	0.59	1.47
2-Ethylhexanol	0.36	0.06	0.47	—

there is a much less clear correlation between surfactant type and the nature of the solubilized material and the degree of additive incorporation.

It has been suggested that, in general, increasing the chain length of an *n*-alkane or *n*-alkyl-substituted benzene reduces its solubilization in a given surfactant solution. While the presence of unsaturation or cyclic structures tends to increase solubilization, branching appears to have little or no effect. Although such observations can be useful for the simple systems considered, more complicated additive structures fail to behave in such an orderly fashion. The addition of one benzene ring, for example, tends to increase solubility, while a second fused ring, such as in naphthalene derivatives, produces the opposite effect.

In summary, the relationship between the chemical structure of the additive and its ability to be incorporated into a surfactant solution is quite complex and has so far not lent itself to simple analysis and structural correlation. Perhaps, as our understanding of the geometric packing requirements of molecules in the micellar core and palisades layer improves, and the importance of molecular interactions among the various constituents is better understood, a more rational scheme for predicting solubilization results will emerge.

8.1.4 The Effect of Temperature on Solubilization Phenomena

When considering the effects of temperature changes on the solubilization process, two areas of concern must be addressed:

- 1) As has been stated often, the ability of a given surfactant to solubilize an additive is intimately related to the characteristics of the micelle (size, shape, ionic nature, etc.). Since changes in temperature are known to affect some of those characteristics, it should not be surprising to find alterations in the solubilizing properties of surfactants as a result of modifications in micellar structure.
- 2) Changes in temperature can affect the intermolecular interactions between solvent and solutes (hydrogen bonding, for example), so the overall solvent properties of the liquid for surfactant and additive may be significantly altered.

Data illustrating the effect of temperature changes on the ability of several alkali soaps to solubilize *N,N*-dimethylaminoazobenzene (DMAB) are shown in Table 8.4. Interestingly, if one considers the relative change (MAC_{50}/MAC_{30}) in the amounts solubilized at 30 and 50 °C, the greatest increase occurs for the system having the lowest initial solubilizing power at the lower temperature. In a relative sense, the effect of the temperature increase can be viewed as the poor getting richer and the rich not doing too badly.

In studies of the effects of temperature changes on the solubilizing power of the nonionic surfactant $CH_3(CH_2)_9(OCH_2CH_2)_{12}OCH_3$ containing fixed amounts of *n*-decane and *n*-decanol, it was found that in the case of each additive, as the temperature was increased, the apparent micellar aggregation number increased, as expected from results in the absence of additives (Table 8.5), and that the number of additive molecules incorporated per micelle increased. However, examination of the data shows that the ratio of surfactant to additive molecules in each micelle remains constant throughout the temperature range, the value being 10 for the *n*-decane solubilized in the micellar core and 2.5 for the *n*-decanol located in the palisades region.

Table 8.4 The effect of temperature on the MAC of DMAB in several surfactant systems.

Surfactant	MAC (g/mol surf.)		
	30°	50°	MAC_{50}/MAC_{30}
$C_9H_{19}COO^- Na^+$	0.64	1.19	1.86
$C_{11}H_{23}COO^- Na^+$	1.50	2.43	1.62
$C_{13}H_{27}COO^- Na^+$	2.71	4.15	1.53
$C_{12}H_{25}NH_3^+ Cl^-$	4.32	5.63	1.30

Table 8.5 The effect of temperature on the micelle size and aggregation number of $\text{CH}_3(\text{CH}_2)_9(\text{OCH}_2\text{CH}_2)_{12}\text{OCH}_3$ containing fixed amounts of *n*-decane and *n*-decanol.

Temperature (°C) additive/micelle	cmc (mM)	Aggregation no	Molecules
<i>n</i> -Decane (1.86 wt. %)			
10	2.36	65	5.9
30	1.50	67	6.1
50	1.11	71	6.5
60	1.0	85	7.8
69	0.89	110	10.1
<i>n</i> -Decanol (9.17 wt. %)			
10	2.07	73	30
30	1.26	83	33
43	1.09	110	44
50	1.00	140	57
55	0.94	186	76
61	0.89	404	163

The effect of temperature changes on the micellization of ionic surfactants is not as simple a relationship as that found for most nonionic materials, and it is to be expected that the effects on solubilization will be correspondingly more complex. It has been reported that micellar solutions of dodecylamine hydrochloride saturated with xylene passed from a clear isotropic solution to a turbid dispersion as the temperature was increased. It was noted in Chapter 6 that many ionic surfactants pass through a minimum in **cmc** near room temperature; it would be interesting to know if a maximum in solubilizing power is attained in the same temperature region as the minimum in **cmc**.

8.1.5 The Effects of Nonelectrolyte Solutes

Nonelectrolyte solutes that are not part of the primary solubilized system (solvent–surfactant–additive) can have a significant effect on the solubilizing power of micellar solutions as a result of their effects on **cmc**'s and aggregation numbers. It has become especially obvious that the addition of polar solutes such as phenols and long-chain alcohols and amines can greatly increase the solubility of nonpolar additives in ionic surfactant solutions. A suggested mechanism for such results based on theories of intra- and intermolecular interactions involves the presumed insertion of polar additive molecules between adjacent surfactant molecules in the micelle (Figure 8.2). As a result of that “spacing” of the ionic groups, repulsive interactions among head groups and unfavorable contact between the aqueous phase and exposed hydrocarbon in the core can be reduced. Those two modifications of the micellar surface would allow a decrease in surface curvature of the micelle and a subsequent increase in the capacity of the core to accommodate solubilized nonpolar additives.

Unlike polar solutes with relatively large hydrophobic tails, short-chain alcohols such as ethanol can significantly reduce the solubilizing power of a surfactant. In the discussion of the effects of such materials on the micellization process from Chapter 6, it was shown that the addition of

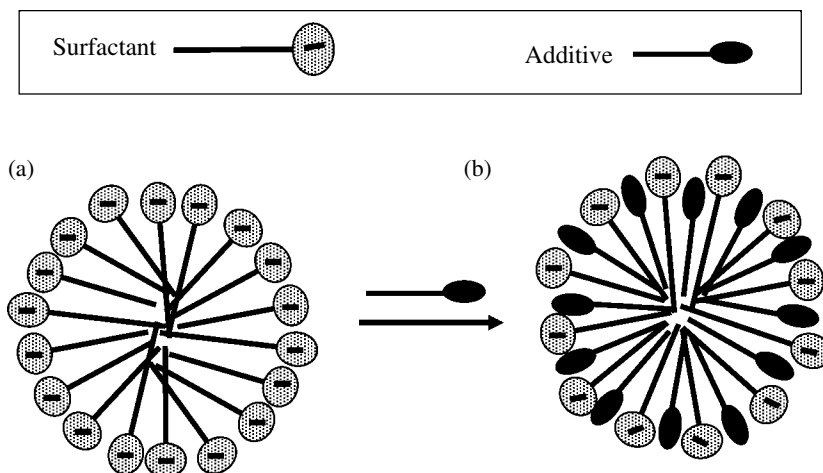


Figure 8.2 Proposed mechanism (the “Winsor” mechanism) for the role of nonpolar additives in increased solubilization in ionic micellar systems (a) head group repulsion in ionic surfactants limits micelle size and solubilizing capacity by increasing the effective area per molecule and (b) the insertion of polar additives between adjacent head groups “insulates” the repulsive interactions between charge groups allowing the micelle to attain a larger radius of curvature and increase its capacity for solubilization.

significant quantities of short-chain alcohols, acetone, dioxane, etc. could result in profound changes in the **cmc** and aggregation number of surfactants, even to the point of completely inhibiting micelle formation. It is understandable, then, that such solutes could also adversely affect the solubilization capacity of a surfactant solution.

From the observations above, it seems clear that the effects of an added nonelectrolyte on the solubilizing capacity of a given surfactant system may be quite complex and may not lend themselves to easy analysis. It can be assumed, however, that the fundamental relationships that exist between the solute and the micellization characteristics of the surfactant, in the absence of the solubilized additive, can be used to good advantage in predicting what may reasonably be expected in the four-component system.

8.1.6 The Effects of Added Electrolyte

The effects of added electrolytes on a micellar system were discussed in Chapter 6. For the case of ionic micelles, the effect of such addition is to decrease the **cmc** and increase the aggregation number. Such changes are predictable in micellar systems and might be expected to produce parallel effects on solubilization. In fact, however, the results are not always so easily analyzed. At surfactant concentrations near the **cmc**, it is usually found that the solubilizing power of a system will increase with the addition of electrolyte, as a result of the greater number of micelles available in the system. At surfactant concentrations well above the **cmc**, however, the simplicity of the relationship between electrolyte concentration, **cmc**, and solubilization seems to disappear.

A study of the solubilization of decanol in solutions of sodium octanoate showed that at low surfactant concentrations the solubilization of the additive increased rapidly after the **cmc** was exceeded and continued to do so for some time as the concentration of sodium chloride was increased. At higher surfactant concentrations, however, it was found that there was an initial increase in decanol incorporation, which reached a maximum then began to decrease as the salt level continued to increase. When the octanoate concentration well exceeded the **cmc**,

the addition of salt resulted in an immediate decrease in the ability of the system to incorporate the additive. Such complex interactions have been attributed to alterations in the thermodynamics of mixed micelle formation for the decanol and carboxylate salt. Similar results may be seen in systems where the increased electrolyte content produces a change in the character of the micellar system: a sphere-to-rod micellar transformation or the development of a mesophase, for example.

Variations in results for the effect of added electrolytes on solubilization by ionic surfactants might also be related to the nature of the additive and its potential location in the micelle. For nonpolar additives or those lying deep in the palisades layer of the micelle, it seems reasonable to expect that the increased volume of the micellar core produced by electrolytes would lead to a greater capacity for solubilization. For more polar materials, which would be expected to be incorporated less deeply in the micelle, added electrolyte results in a closer packing of ionic head groups, which could reduce the available space for solubilized molecules. Changes in micelle shape, from spheres to rods, for example, would also cause less surface volume to be available in the palisades layer as a result of closer packing of the head groups or, put another way, less curvature in the layer.

In the case of nonionic surfactants, the effects of added electrolytes seem to parallel their effects on the micellization process. When such addition produces an increase in micellar aggregation number, an increase in solubilizing capacity for hydrocarbon additives is also found. The results for the solubilization of polar materials are, again, less clear-cut. A similar trend is generally found for cationic and amphoteric surfactants.

8.1.7 Miscellaneous Factors Affecting Micellar Solubilization

Other factors that can affect the ability of a particular surfactant system to solubilize materials include pH and pressure. The effects of such factors, however, have not been as extensively reported in the literature as the factors discussed above, and they are often very specific to each surfactant system. Obviously, surfactants that show special sensitivity to pH such as the carboxylate salts will also be expected to exhibit significant changes in solubilization with changes in that factor. In addition, changes in pH can affect the nature of the additive itself, producing dramatic changes in its interactions with the micelle, including the locus of solubilization. Such effects can be especially important in many applications of solubilization, especially in the pharmaceutical field.

The effects of such a variable as pressure on micelle formation and solubilization are a relatively new field of investigation. It can be assumed that significant effects will be observed once sufficient pressures have been attained. However, such levels lie outside the normally available range of experimental conditions and are of little practical concern except in studies of surfactant activity in supercritical fluid processes.

8.1.8 Hydrotropes

The unique chemical structures that result in their exhibiting significant surface activity do so because of the balance between the hydrophilic and hydrophobic portions of the molecule. There are also many compounds with the same basic combinations of units with the same distribution that do not exhibit sufficient surface activity to be classed as surfactants. Many of those compounds fall into the category termed “hydrotropes.” A hydrotrope is a compound that solubilizes hydrophobic compounds in aqueous solutions by means other than micellar solubilization since they do not form micelles. Typically, hydrotropes consist of a hydrophilic part and a hydrophobic part (like surfactants), but the hydrophobic part is generally too small to cause spontaneous self-aggregation.

Hydrotropes do not have critical concentrations above which self-aggregation starts to occur as happens with micelle- and vesicle-forming surfactants, which have a specific, well determined **cmc** or a critical concentration at which vesicle formation begins. Instead, some hydrotropes aggregate in a stepwise aggregation process, gradually increasing aggregation size. In fact, many hydrotropes do not seem to self-aggregate at all, unless a hydrophobic solute is added.

Hydrotropes, while not widely known outside very limited industrial and academic areas, are used in various industrial, pharmaceutical, and biomedical applications. Examples of common hydrotropes include urea, toluene and xylene sulfonic acid salts, cumene sulfonic acid salts, and several natural compounds such as adenosine triphosphate (ATP). ATP has been found to be an especially efficient in preventing the aggregation of proteins at normal physiologic concentrations and to be approximately an order of magnitude more effective than sodium xylene sulfonate in a standard hydrotrope evaluation assay. The activity of ATP was found to be independent of its activity as an energy moderator in cellular activity.

The term “hydrotropy” was originally coined to indicate an increase in the solubility of a solute by the addition of fairly high concentrations of alkali metal salts of various organic acids. However, the term has been used to designate non-micelle-forming substances, either liquids or solids, organic or inorganic, capable of solubilizing insoluble compounds.

The chemical structure of the conventional hydrotropic salts (prototype, sodium benzoate) consists generally of two essential parts, an anionic group and a hydrophobic aromatic ring or ring system. The anionic group is involved in bringing about high aqueous solubility, which is a prerequisite for a hydrotropic substance. The type of anion or metal ion appeared to have a minor effect on the phenomenon. On the other hand, planarity of the hydrophobic part has been emphasized as an important factor in the mechanism of hydrotropic solubilization. Figure 8.3 shows the structures of several typical hydrotropes in current use.

The addition of hydrotropes to many cleaning and personal care products allows for the formulation of products with higher concentrations of surfactants and other components than would be otherwise practical. Their small to moderate quantities, usually 0.1–15%, stabilize a formulation, modify the cloud point of nonionic surfactants, modify viscosity, reduce or prevent phase separation at low temperatures, and limit foaming. Typical applications include liquid soaps, dishwashing detergents, surface cleaners, laundry detergents, liquid hand soaps, and hair care products. They have also found use in biomedical research because they are able to more effectively stabilize protein extracts extracted from cell membranes.

Because of their widespread use in commercial products like those mentioned, their environmental impact has been extensively investigated. Their potential for harmful bioaccumulation

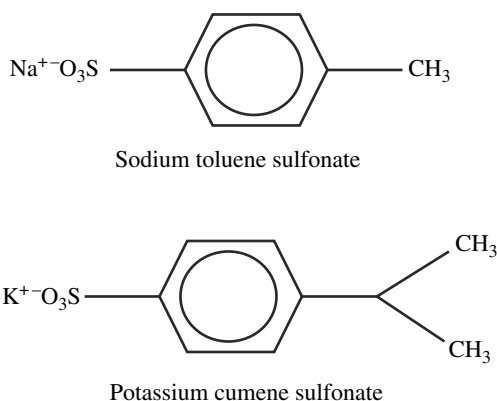


Figure 8.3 Structures of two commonly used hydrotropes.

has been found to be small. They are generally of low volatility, are readily biodegradable, and can be efficiently removed by secondary water treatment processes. Their toxicity has been determined to be very low and has not found to be mutagenic or carcinogenic or to have reproductive toxicity. They are therefore considered to be of no environmental concern at present levels of use.

8.2 Micellar Catalysis

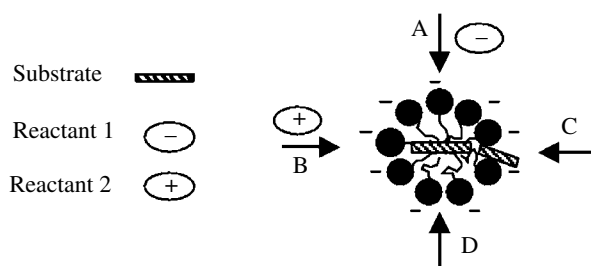
It is well recognized in all branches of chemistry that the rate of a chemical reaction can be very sensitive to the nature of the reaction environment. Reactions involving polar or ionic transition states can be especially sensitive to the polarity of the reaction medium. It should not be too surprising, then, that many chemical reactions, especially those in which one reactant may be soluble in water and the other in oil, can exhibit a significant enhancement in rate when carried out in the presence of surfactant micelles. The presence of the micellar species can provide a beneficial effect through two possible mechanisms:

- 1) The region of the micelle where the two immiscible phases interact, sometimes referred to as the “palisades region” of the micelle, represents a transition zone between a polar aqueous environment, which may be either the bulk phase or the micellar core, and a nonpolar hydrophobic region. Such a gradient in polarity can serve as a convenient area of intermediate polarity suitable for increased reactant interaction or for optimizing the energy of transition state formation.
- 2) The potential for the micelle to solubilize a reactant that would not normally have significant solubility in the reaction medium means that it can serve as a ready reservoir of reactant, in effect increasing the available concentrations of reactants (Figure 8.4). Reaction rate enhancements as high as 10^5 have been reported for some micellar systems, which makes such systems very attractive for potential practical applications.

8.2.1 Micellar Catalysis in Aqueous Solution

In aqueous media, a micellar system can serve as a catalyst for organic reactions, but it is also possible for it to retard such reactions. Two possible mechanisms for catalytic action were suggested above: inhibitory actions may arise from unfavorable electrostatic interactions between reactants

Figure 8.4 Proposed mechanisms for the catalytic (and retarding) effects of micelles in organic reactions.



- A – Reactant of same sign impeded approach: slow reaction
- B – Reactant of opposite sign: accelerated reaction
- C – Solubilization in palisades improves solvent character
- D – Increased substrate availability due to solubilization

and changes in the distribution of reactants between the bulk and micellar phases. In the case of electrostatic inhibition, the presence of a charge on the micelle surface can have two effects on a reaction involving a charged species. In the base hydrolysis of water-insoluble esters, for example, if the micelle charge is negative, the transport of hydroxide ion into or through the palisades layer will be retarded by charge repulsion. If the micelle is positively charged, the inclusion of the oppositely charged species will be facilitated. For nonionic and zwitterionic surfactants, there will be little or no effect as a result of electrostatic interactions. Although such a model of electrostatic effects is simple, it has generally been supported by experiment. The basic hydrolysis of esters, for example, is catalyzed by cationic and inhibited by anionic surfactants, while the opposite is true for the acid hydrolysis of orthoesters. Nonionic and zwitterionic surfactants can also produce significant rate enhancement, indicating that hydrophobic effects can, in some instances, predominate over electrostatics.

The ability of a micellar system to solubilize a reactant may affect its action as a catalyst or inhibitor in a reaction. When a surfactant system serves as a reservoir for increasing the availability of one reactant, any change that increases the solubilizing capacity of the micelle should also increase its effectiveness as a catalysis. If, on the other hand, the reaction must occur in the bulk phase, increased solubilizing power may remove reactant from the reaction medium and therefore decrease catalytic or increase inhibitor efficiency. As for many things in the world, there can be too much of a good thing in any situation.

In aqueous solution, the effectiveness of micellar systems as catalysts is quite often found to increase with the length of the alkyl chain. It has been found, for example, that the rate of hydrolysis of methyl orthobenzoate in the presence of sodium alkyl sulfates increased in the order octyl < decyl < dodecyl < tetradecyl < hexadecyl. Such a result may be attributed to either electrostatic or solubilizing effects. Since, as a general rule, the aggregation number of aqueous micelles increases with the chain length in a homologous series, there must be a parallel increase in the surface charge density at the micelle surface. It might be expected, then, that any effects due to electrostatic interactions would also increase. If the hydrolysis is acid catalyzed, an electrostatic enhancement of the reaction rate would be expected; the base-catalyzed reaction would be expected to be slower. Alternatively (or additionally), the larger aggregation number results in an increase in the solubilizing power of the system with a resulting rate increase due to increased substrate availability. The importance of each mechanism will depend on the specifics of the reaction.

In addition to the effects noted for increases in the charge density on the micelle, the charge density on the individual surfactant molecules can be important. It has been found, for example, that cationic surfactants containing two charge groups were significantly better at increasing the rate of nucleophilic aromatic substitutions than analogous singly charged materials. Similar results have been noted for singly versus doubly charged anionic surfactants.

As might be expected, the structure of the reactive substrate can have as much influence on micelle-assisted rate enhancement as that of the surfactant. Since the catalytic effectiveness of the micelle can be related to the location and orientation of the substrate in the micellar structure, the more hydrophobic the substrate (and the surfactant), the more significant may be the catalytic effect.

When non-surfactant co-solutes are added to the micellar reaction mixture, the results can be quite unpredictable. Studies have found that the presence of excess surfactant counterions or common ions retards the catalytic activity of the micelle, with larger ions being more effective in that respect. In contrast, the addition of neutral electrolyte has been found to enhance micellar catalysis in some instances while showing little or no effect in others. It has been proposed that the

retardation effect of excess common counterions is due to a competition between the excess ions and the reactive substrate most closely associated with the micelle for the available positions or “binding sites” on or in the micelle. The enhancing effect, however, has been attributed to the more general effects of added electrolyte on the properties of micelles, that is, lowering of the **cmc**, increasing the aggregation number, etc., all of which often tend to increase catalytic activity.

As new experimental techniques produce more detailed information on the location of the various components in micellar systems and the thermodynamics of substrate–micelle interactions become better understood, our ability to expand the applicability of such systems based upon good science and good judgment will be greatly enhanced.

8.2.2 Micellar Catalysis in Nonaqueous Solvents

As previously noted, interactions between polar head groups in nonaqueous solvents provide the primary driving force for the formation of inverted or reversed micellar aggregates in such media. The nature of such reversed micellar cores is such that they provide a unique location for the solubilization of polar substrates. While keeping in mind the potentially dramatic effects of additives on the properties of micellar solutions, it is obvious that such nonaqueous systems hold great potential from a catalytic standpoint.

One of the first reported instances of catalysis by reversed micelles in the early 1970s concerned the hydrolysis of *p*-nitrophenyl dodecanoate in hexanol–water systems containing cetyltrimethylammonium bromide (CTAB). Since that time, nonaqueous systems have gained greater attention as models that mimic the catalytic activity of natural enzymatic reactions. The fundamental principles controlling activity in nonaqueous systems are basically the same as those for aqueous solutions, except that the specificity of the micellar core for the solubilization of polar substrates is much greater for the nonaqueous situation. The popularity of reversed micelles as models for enzyme catalysis stems from the fact that the micellar core is capable of binding substrates in concentrations and orientations that can be very specific to certain functionalities, much as an enzyme would do. As a result, reaction rate enhancements can be obtained comparable with those of the natural systems and far in excess of what can be explained on the basis of the partitioning or availability of substrate.

Work in the area of micellar catalysis in both aqueous and nonaqueous solvent systems is certain to continue to grow in importance as a tool for better understanding the chemistry and mechanics of enzymatic catalysis, as a probe for studying the mechanistic aspects of many reactions, and as a route to improved yields in reactions of academic interest. Of more practical significance, however, may be the expanding use of micellar catalysis in industrial applications as a method for obtaining maximum production with minimum input of time, energy, and materials.

9

Polymeric Surfactants and Surfactant–Polymer Interactions

A glance at ingredients lists of many consumer products will quickly show that surfactants constitute some of the functionally most important ingredients in cosmetic and toiletry products, foods, coatings, pharmaceuticals, and many other systems of wide economic and technological importance. In many, if not most, of those applications, polymeric materials, either natural or synthetic, are present in the final product formulations or in the ultimate targets for their use. Other surfactant applications, especially in the medical and biological fields, also potentially involve the interaction of polymers (including proteins, carbohydrates, nucleosides, etc.) with surfactant-containing systems. In addition, many natural and synthetic polymers are themselves amphiphilic, or potentially so, so one must consider not only the surface activity of a “normal” surfactant in a system but also that of any polymeric species present. Not surprisingly, the situation can become very interesting as a system becomes more complicated in terms of the addition of amphiphilic materials. This chapter will present some of the basic aspects of normal amphiphile–polymer interactions, an introduction to the subject of polymeric surfactants, and some of the potential complications that might arise in the presence of both types of amphiphiles.

9.1 Polymeric Surfactants and Amphiphiles

Polymers can generally be categorized into classifications based on their specific chemical makeup (monomer content) and the exact manner in which the monomers are arranged along the polymer chain. Within each class there are finer subdivisions based on the presence or absence of branching along the chain and the stereochemical relationship among the monomer units. Since polymer chemistry is a vast area of colloid science or material science, as one prefers, the current discussion will be limited to the primary chemical structure of polymers with the more refined aspects being left for other venues.

The general classes of polymers can be defined as follows:

- 1) *Homopolymers*, in which all of the monomer units are identical.
- 2) *Heteropolymers* or *random copolymers*, in which at least two different monomer units are arranged in a more or less random manner along the chain.
- 3) *Block copolymers*, in which different monomer units are linked in homogeneous groups to make up the chain.
- 4) *Graft* or “comb” *copolymers*, in which different monomer units are grafted onto a main chain or backbone to form a comb-like structure.

- 5) *Polyelectrolytes* that can be members of any of the above classes, but with the characteristic that they carry a significant number of electrical charges along the chain that impart special characteristics to the class.

Schematic representations of the five classes are shown in Figure 9.1. The representations given are intended to be illustrative and in no way show the true complexity of most polymer chains. The polymer structures illustrated in the figure are generally synthetic, but natural polymers can also fall into the same categories.

Polymers such as cellulose, starches, natural gums, acrylates, acrylamides, polyethyleneimines, and pyrrolidones have been staples of the water-soluble polymer industry for many years. In an attempt to expand the basic utility of such materials and to solve certain technological needs not satisfied by more conventional amphiphilic materials, they have been modified to give special performance additives in commercial applications. Coming from the opposite direction in terms of solubility, hydrophobic polymers such as polystyrene, A–B block copolymers, A–B–A–B alternating copolymers, and random copolymers can be functionalized to increase their hydrophilicity. Chemical structures of some of the more common candidates for functionalization are shown in Figure 9.2.

Polymers of those and other families can be modified to increase their hydrophobic or hydrophilic characters and are finding increasing use in the formulation of consumer products and in industrial operations. While their end-use performance depends on the nature and degree of functionalization and the basic nature of the base polymer backbone, the relationship between

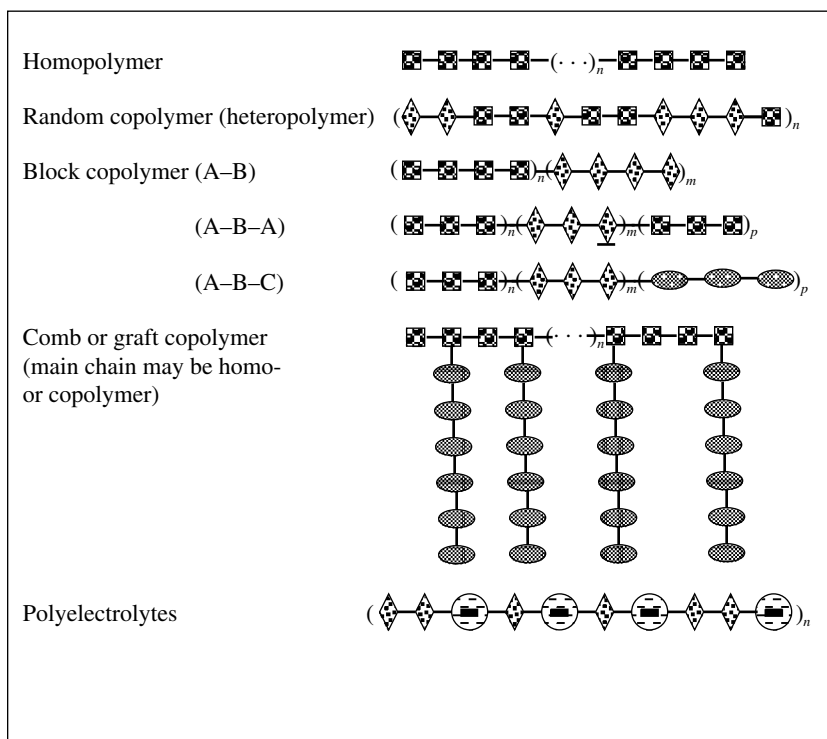


Figure 9.1 Schematic representations of the four general classes of polymers, where A, B, C, etc. represent different monomer units.

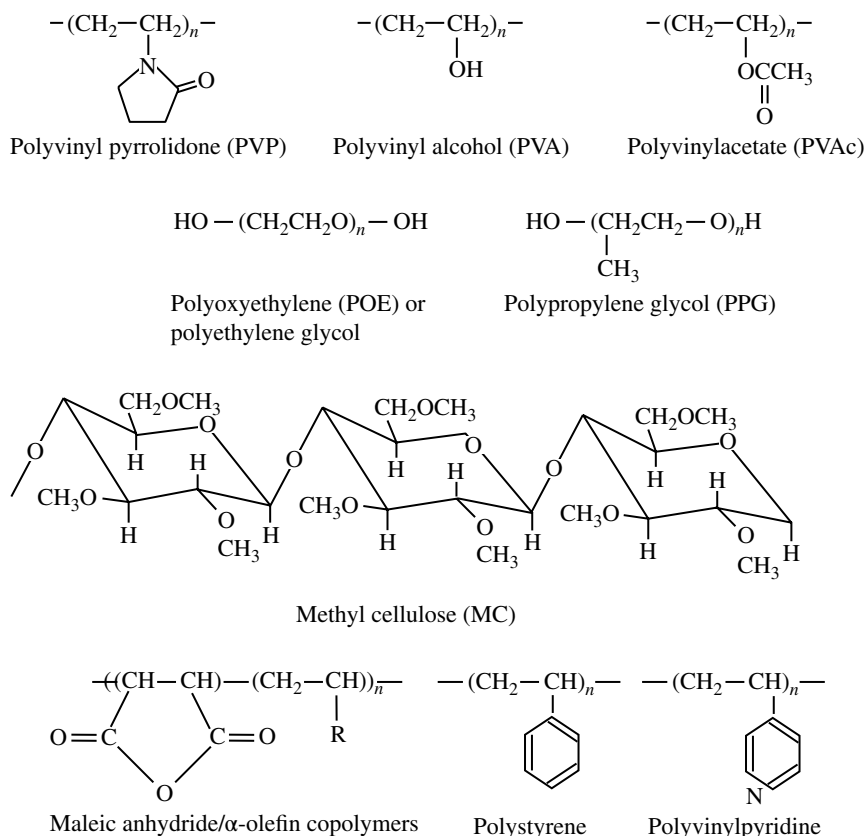


Figure 9.2 Some basic chemical structures of common polymers used in the preparation of polymeric surfactants.

structural modifications and performance is not yet sufficiently understood to allow sweeping generalizations about structure–performance relationships similar to those generally applied to monomeric surfactants. Many of the same basic concepts are found to apply, however, so the formulator looking into the use of such materials will not always start out working in the dark.

9.2 Some Basic Chemistry of Polymeric Surfactant Synthesis

As noted above, many classes of water-soluble and water-insoluble polymers can be functionalized to increase their hydrophobicity or hydrophilicity, as needed. In some cases, the resulting materials will be statistically random modifications, while in other cases the distribution of the relevant functional modifications will be more regular or uniform.

9.2.1 The Modification of Natural Cellulosic Materials, Gums, and Proteins

Natural product polymers such as cellulose, starches, gums, and proteins have been employed in a wide variety of applications for centuries. In many cases, particularly in the cases of gums and some proteins, the natural product is amphiphilic as isolated and can be used directly. While such

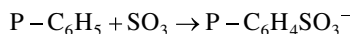
“natural” amphiphilic materials have found wide use in the food, cosmetic, and pharmaceutical industries, as well as in industrial process applications, more stringent environmental, regulatory, and end-use requirements of modern products often require new modified products that, in some minds at least, take them out of the “natural” category. Semantic nit-picking aside, modified natural polymers have a number of inherent advantages, including their generally lower environmental load in manufacture, their enhanced biodegradability because of their sources, and the theoretically renewable nature of their sources.

The modification of natural polymers to introduce or modify their amphiphilic character can take three general approaches: (i) degradation processes such as hydrolysis to reduce molecular weights or break cross-linking bonds to increase water solubility in normally insoluble materials such as cellulose; (ii) chemical modification through the addition of molecular components that alter the nature of the molecules, usually involving esterification, amination, oxidation, etherification, or similar reactions; and (iii) enzymatic modifications.

A classical example of such functionalization is the carboxymethylation of cellulose to produce carboxymethylcellulose (CMC), used in a wide variety of applications as a thickener, stabilizer, binder, etc. The functional characteristics of such materials can be controlled with some exactness by controlling the degree of functionalization and the molecular weight of the base polymer. Similar classes of materials can be prepared by the hydrolysis of proteins or the use of various reactions well known to the organic chemist.

9.2.2 Synthetic Polymeric Surfactants

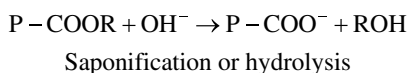
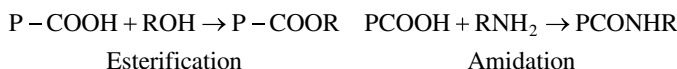
Synthetic polymers can be equally useful as bases for the preparation of polymeric amphiphilic materials. A common example of the functionalization of a water-insoluble material is the sulfonation of polystyrene:



where P represents a polymer chain. Depending on the degree of sulfonation attained, such materials can remain water insoluble, but with sufficient electrical charge to make them useful as binding reagents, or they can attain such a high charge that they dissolve or at least swell substantially in aqueous solution. In the form of cross-linked particles, sulfonated polystyrenes produce swollen microgel particles that find wide application as ion exchange resins. Other derivatives of polystyrene and other aromatic polymers can be prepared by any number of standard organic reaction schemes to produce other anionic or cationic polymers. Special reactive units can also be attached to the polymer side chain that will, for example, bind specific antibodies for special applications. The sulfonation and derivatization of most water-insoluble polymers are essentially random processes, so the exact distribution of charges or other modifications along the polymer chain will be somewhat variable. Close process control can, however, ensure a functionally reproducible product.

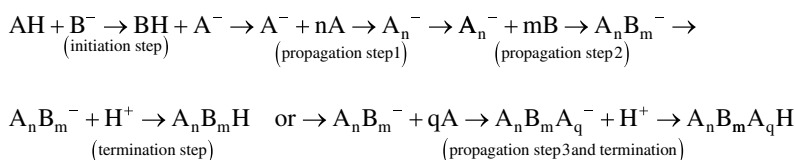
Polyacrylic acid and polyacrylamide are typical water-soluble polymers that can be functionalized by the addition of hydrophobic side chains that turn them into amphiphilic materials. The usual processes would include esterification and amidation of the carboxyl groups. Similar results can be obtained by preparing copolymers of acrylic and methacrylic acid with the desired preformed esters. A third alternative is the formation of polyacrylate or polymethacrylate esters followed by controlled saponification or hydrolysis to a desired degree of free carboxyl groups. The derivatization of acrylics is also an essentially random process, so the exact characteristics of

the final product may be somewhat variable. Close process control can, again, ensure a functionally reproducible product.



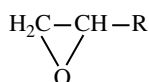
An interesting class of polymers that can be functionalized in a more regular manner are alternating A-B polymers prepared, for example, by the reaction of maleic anhydride with terminal or α -alkenes discussed below.

Perhaps the most common and well-studied regular polymeric surfactant family is that of the block copolymers. Denoting one monomer type as A and the other as B, typical basic compositions would be A-B, A-B-A, and B-A-B. The chemistry and technology for preparing such polymers is well developed. The most common addition process essentially involves a multistep reaction sequence in which one monomer (A, for example) is reacted with an acid or base catalyst to produce a homopolymer with a reactive terminal unit (A_n^-). When monomer A is used up or reacted to the desired extent, the reaction is treated with monomer B, which then begins to polymerize on the active terminal of A_n^- . After a suitable reaction time, the polymerization can be terminated to produce the $\text{A}_n\text{-B}_m$ copolymer, or a second addition of A to A_nB_m^- will produce the A-B-A family. The amphiphilic properties of the resulting product will depend on the relative amounts of A and B added and, to some extent, the order of addition. The process is illustrated schematically for a base-catalyzed addition process as



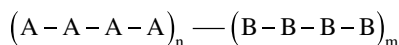
The description here is, of course, very simplified. In reality, the process requires a great deal of technological skill; it is, nevertheless, quite achievable with a little work. In a few cases in which the reactivity of two monomers are very different, block copolymers can be prepared by a simpler free radical polymerization process.

In block copolymers, the careful control of monomer feed and reaction conditions allows the preparation of surfactants in which such characteristics as the hydrophile-lipophile balance (HLB), solubility, wetting, and foaming properties can be closely and reproducibly controlled. The classification of these surfactants is primarily based on the nature of the initiator employed in the formation of the initial polymer block, with subclasses determined by the compositions of the various blocks. In fact, there is no need for the initiator in these materials to be particularly hydrophobic; the hydrophobicity is derived from one of the two polymeric blocks. Typical initiators would be monohydric alcohols such as butanol and dihydric materials (glycol, glycerol and higher polyols, ethylene diamine, etc.). A generic alkylene oxide molecule can be represented by

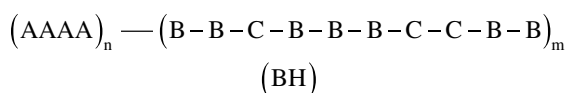


where R = H (ethylene oxide), R = CH₃ (propylene oxide), etc. It is theoretically possible to use di-, tri-, and even tetra-substituted oxides, either symmetrically or asymmetrically substituted, although they are less common due to higher costs and poorer reactivity.

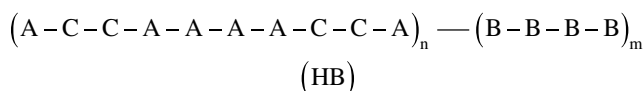
It is possible to envisage four subclasses of surfactants in this group based on the nature of the polymer blocks in the molecule. The first and simplest is that in which each block is homogeneous; that is, a single alkylene oxide is used in the monomer feed during each step in the preparation to give a species of the form



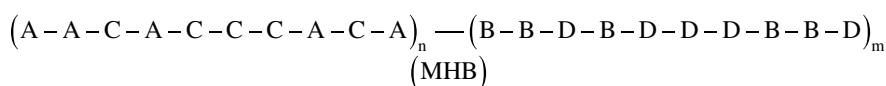
where A and B designate different alkyl oxide starting materials. Such polymers will be referred to as all-block (AB) surfactants. A second subclass is termed the block-heteric (BH) or heteric-block (HB) nonionics:



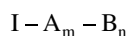
or



in which one portion of the molecule is composed of a single alkylene oxide while the other is a mixture of two or more such materials, one of which (C) may be the same as that of the homogeneous block portion of the molecule. In the preparation of such materials, the hetero portion of the molecule will be totally random. The properties of BH and HB surfactants will be different from those of the AB surfactants. The fourth subclass will be that in which both steps in the preparation involve the addition of mixtures of alkylene oxides to give mixed heteric-block (MHB) materials with the schematic structure



In the preparation of the AB surfactants, a monofunctional initiator (i.e. one having a single acidic hydrogen) such as a monohydric alcohol (ROH), an acid (RCOOH), a mercaptan (RSH), a secondary amine (RR'NH), or an *N*-substituted amide (RCONR'H) is employed as the initiator. A controlled feed of the A oxide is added to obtain the desired average degree of polymerization, *m*, after which the feed of the B oxide is started. Such materials would generally be given by the formula



where I is the initiator molecule. For purposes of discussion, the A portion is an alkylene oxide unit in which at least one hydrogen of the alkylene oxide has been replaced by an alkyl or aryl group, and *m* is the degree of polymerization, usually greater than six. The B linkage would then be a hydrophilic group such as polyoxyethylene, with *n* again being the average degree of polymerization.

The most common commercially available members of this family are the polyoxypropylene-polyoxyethylene (POP-POE) block copolymers, widely known as “poloxamers.” A wide range of surfactant properties can be achieved by the proper control of *m* and *n*. The best known members of this family are the “Pluronics” that offer a wide range of products composed of blocks of ethylene oxide and propylene oxide with various chain lengths of each component. They offer a wide selection of physical forms, solubilities, and HLB numbers allowing a wide selection of possible solutions to surfactant needs.

The other subclasses of block polymer surfactants, BH, HB, and MHB, are prepared essentially the same way. The major difference is that the monomer feed for the alkylene oxide in each step will be:

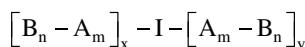
For BH materials – pure A followed by B + C.

For HB materials – A + C followed by pure B.

For MHB materials – A + C followed by B + D.

The H-blocks will be random copolymers reflecting the composition of the oxide feed with its solubility characteristics determined by the relative ratios of potentially water-soluble and water-insoluble materials. These materials have a potential manufacturing advantage in that it is possible to vary the monomer feed composition during the reaction to continuously change the composition of the growing polymer chain. That is, as the reaction is being carried out, the number of each type of alkylene oxide available for addition to the growing chain changes, and the chain composition changes accordingly. In this way, the resultant material may possess a high proportion of hydrophobic (or hydrophilic) units near the initiator, with a smooth transition to hydrophilic (or hydrophobic) toward the terminus of the chain.

It is also possible to employ multifunctional initiators to prepare AB surfactants of the form



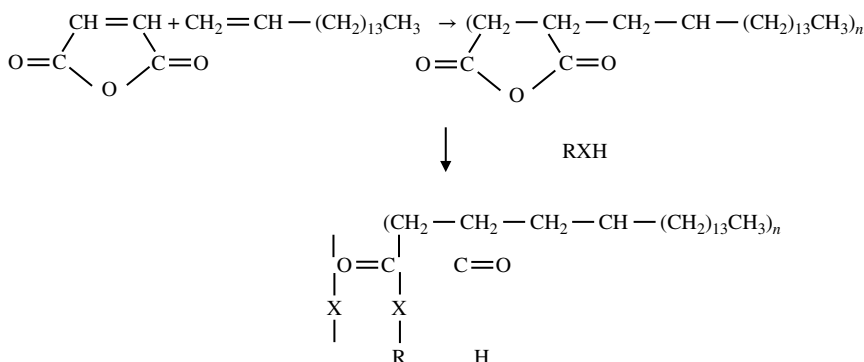
where *x* and *y* may be 1, 2, Multifunctional initiators can also be employed in materials of BH, HB, and MHB types, although the chemistry and engineering for the commercial production of such materials could get a bit involved.

Probably the most studied and used members of the block copolymer surfactants are members of the POP-POE family. A wide range of materials have been developed industrially that range from oil-soluble to highly water-soluble materials. The surfactant characteristics of each member of the family have been well documented so that the formulator can usually determine relatively quickly which product, if any, best suits her needs.

It is also possible to use functionalities other than alkylene oxides in the preparation of the polymer block surfactants (polyamines, for example); however, there has been much less published about activity in that area.

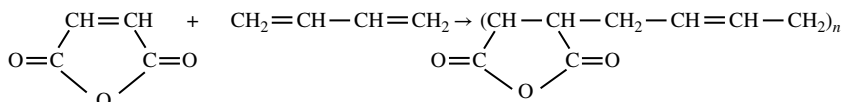
Polymeric nonionic surfactants can also be prepared from prepolymerized hydrocarbon backbones. An interesting class of materials already mentioned, alternating copolymers, can be synthesized from polymers of maleic anhydride and styrene, α -olefins, and other interesting molecules. Maleic anhydride has the interesting (and useful) property that it tends to copolymerize with most other olefins in a regularly alternating manner: $MA + O \rightarrow (MA-O)_n$, where MA represents the maleic anhydride unit and O the olefin component. An example of such a synthesis would be the reaction of maleic anhydride with 1-hexadecene. The resulting polyanhydride can be further reacted with an alcohol, amine, etc. (RXH) to produce a “comb” polymer. If the “teeth” of the comb

are, for example, short- to medium-length POE chains, the resulting material is a potentially interesting nonionic comb polymer surfactant:



The production of the half ester of the maleic acid group (only one RX group added per anhydride) leaves a free carboxylic acid just waiting to be reacted or neutralized to produce a new member of the family. As is often the case, the variety of surfactants attainable within a given group is sometimes limited only by the imagination of the synthetic organic chemist.

Another interesting possibility is the reaction of maleic anhydride with butadiene to give an unsaturated polymer backbone that can be further derivatized through the remaining ethylenic linkage:



It is also possible to functionalize random polymers to produce interesting surfactant species, but they do not seem quite so “elegant.”

The discussion so far has been confined to hydrocarbon-based initiators and block groups. There is no fundamental reason for not including materials of other types in the construction of such surfactants. Fluorine-substituted carbon chains, poly-siloxanes, and fluorinated poly-siloxanes have become of increasing interest technologically because of their exceptional surface activity and utility in a wide variety of solvents and chemical environments. General interest in such materials is limited by the lack of reactive starting materials, difficulties in working with such materials (toxicity, etc.), and costs.

Polymeric biosurfactants have begun to receive attention because of their renewable source and potential natural compatibility for use in medical and pharmaceutical applications. They may be produced and extracted from a number of microbiological sources and have indicated great potential utility in specific applications. Since they are generally produced as products of fermentation processes, their cost, for now at least, may preclude their wide application in general industrial or commercial products. It has also been found that the exact structure of the amphiphilic material produced and the overall yield of useful product can be highly sensitive to the characteristics of the source and the nature of the nutrients employed in the fermentation. The complexity of their chemical structures also makes biosurfactants hard to study at the level of basic interfacial chemistry.

9.3 Polymeric Surfactants at Interfaces: Structure and Methodology

This section will introduce some of the basic factors controlling the behavior and function of polymeric surfactants in solution and in colloidal systems. Polymeric surfactants, in principle at least, can perform all the same functions of “normal” surfactants, the main differences between the two being the large difference in molecular mass between the two classes of materials, the higher-order structural conformations found for polymeric materials in solution, and the energetic and kinetic consequences of those conformations and changes to them imparted by changes in the complete functional system.

Certain classes of polymeric surfactants are found to associate in solution to give micelles, while others seem to prefer the solitary life of the lone, coiled polymer chain. Polymeric surfactant micelles can apparently perform most of the functions of normal micelles, including the solubilization of materials such as drugs, or they can associate into higher-level structures to give large changes in viscosity that are useful for stabilizing colloidal dispersions. Although a great deal of information is not readily available, it may be assumed that at least some polymeric systems can form the equivalents of the mesophases found for normal surfactants. For a typical A–B block copolymer, a single-chain micelle may be pictured as shown in Figure 9.3, where the A-units (heavy line) are hydrophobic and the B-units (light lines) are hydrophilic. A similar picture can be used for protein micelles or globules where the different portions of the chain are sufficiently different in terms of their hydrophobic–hydrophilic character.

Polymeric surfactants adsorb at solid–liquid interfaces to give enhanced colloidal stability and at liquid–fluid interfaces to control (increase or inhibit) foaming or emulsion stability. The relatively wide molecular weight distribution of most commercial polymeric surfactants mean that competitive adsorption processes can affect and be affected by other components in a formulation, as well as the end-use function of the system. With polymers, it often takes patience to know the final effect they produce.

Polymeric surfactants in general react to the same changes in solution properties as “normal” surfactants. Changing solution conditions such as temperature, electrolyte concentration and type (i.e. monovalent vs. polyvalent), or the addition of nonelectrolyte solutes will usually result in some alteration of the characteristics of the system related to surfactant properties. That may be especially true of charged materials or polyelectrolytes. Being polymers, however, they also undergo complex conformational changes in solution that often respond to the same or different influences, and those conformational changes will almost certainly alter to some extent the

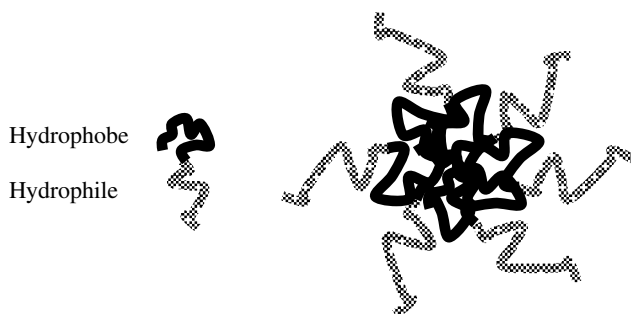


Figure 9.3 A schematic model of an A–B block copolymer micelle.

surfactant properties of the material. Obviously, the complications of polymer solution characteristics superimposed on surfactant solution properties promise an interesting life to the intrepid voyager into the realm. Nevertheless, nature also usually provides a solution, and we find that materials or systems can usually be designed that are either resistant to many of the potential complications or that can actually take advantage of them to produce novel and useful effects.

9.4 The Interactions of “Normal” Surfactants with Polymers

Interactions between surfactants and natural and synthetic polymers have been studied for many years because they are vitally important to the success of product formulations in many areas. Although the basic mechanisms of interaction are reasonably well understood, there still exists disagreement on the details some of the surfactant–polymer interactions at the molecular level. Observations on changes in the interfacial, rheological, spectroscopic, and other physicochemical properties of surfactant systems containing polymers indicate that such interactions, regardless of the exact molecular explanation, can significantly alter the macroscopic characteristics of the system and ultimately its end-use functionality.

It is generally accepted that surfactant–polymer interactions may occur between individual surfactant molecules and the polymer chain (i.e. simple adsorption), or it may occur in the form of polymer–surfactant aggregate complexes. In the latter case, there may be a complex formation between the polymer chain and micelles, pre-micellar or sub-micellar aggregates, liquid crystals, and bicontinuous phases – that is, with any and all of the various surfactant aggregate structures described in Chapters 6 and 7. Other association mechanisms may result in the direct formation of what are sometimes called “hemimicelles” along the polymer chain. The term *hemimicelle* may be defined, for present purposes, as a surfactant aggregate formed in the presence of a polymer chain or solid surface having many of the characteristics of a micelle but being intimately associated with the locus of formation; hemimicelles obviously cannot exist as such in solution. The formation of such structures in surfactant–polymer systems is often illustrated as resembling a string of pearls or water droplets on a spider’s web (Figure 9.4). It could also be hypothesized that hemimicelle structures could form on solid surfaces, especially heterogeneous surfaces that offer variations in the hydrophobic–hydrophilic environments available to interested surfactant molecules. The existence of such aggregates is still speculative, but surface chemistry still has a few ideas to teach us.

The basic forces controlling surfactant interactions with polymers are the same as those involved in other solution or interfacial properties of amphiphilic systems, namely, van der Waals and dispersion forces, the hydrophobic effect, dipolar and acid–base interactions, and electrostatic interactions. The relative importance of each type of interaction will vary with the natures of the

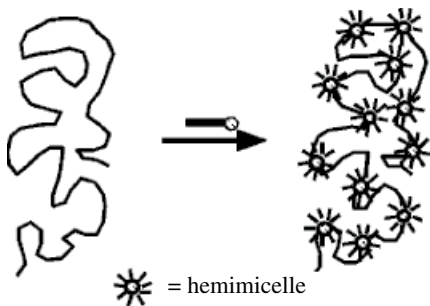


Figure 9.4 “String of pearls” hemimicelle formation along a polymer chain.

polymer and surfactant, so the exact characters of the complexes formed may be almost as varied as the types of material available for study.

Experimental methods for investigating polymer–surfactant interactions vary widely, but they generally fall into two categories: those that measure macroscopic properties of a system such as viscosity, conductivity, dye solubilization, etc. and those that detect changes in the molecular environment of the interacting species such as nuclear magnetic resonance, optical rotary dispersion, circular dichroism, etc. A comparison of the experimental results of various studies can be complicated by variations in the sensitivity of experimental techniques and the physical manifestations of the interactions occurring, as well as differences in the purity and characterization of the experimental components. The results of each experimental approach, while being useful in understanding the “symptoms” of surfactant–polymer interactions, do not always provide an unequivocal distinction among the possible mechanisms at the molecular level. Newer techniques such as small-angle neutron scattering, which come close to “photographing” the relative relationships among polymer and surfactant units, promise to clarify many questions now in dispute. Unfortunately, it is not possible to purchase the required equipment out of the usual laboratory supplier’s catalogues.

9.4.1 Surfactant–Polymer Complex Formation

When a surfactant is added to a polymer solution, it is often observed that processes such as micellization appear to begin at surfactant concentrations below the **cmc** of the material in the absence of polymer. In many cases, a complex aggregate structure is formed in association with the polymer coil at a concentration sometimes referred to as the “critical aggregation concentration” (**cac**), where **cac** < **cmc**, and varies with the nature of the amphiphile and the polymer (Table 9.1). It can be seen from the table that the difference between **cac** and **cmc** can vary by a factor of 10–1000 in some cases.

It is assumed, based on experimental data, that the complex formed in these cases is between the polymer chain and a micelle or micelle-like structure. The significant differences between the **cac**’s and **cmc**’s is attributed to a stabilization of the aggregate structure by the polymer units. In the case of nonionic polymers such as PVP and POE, it might be assumed that the basic interaction is the hydrophobic interaction of the surfactant tail with the polymer chain.

The model of the aggregate would then be the string of pearls already mentioned. In the case of ionic polymers of charge opposite to that of the amphiphile, it would be very surprising if the basic

Table 9.1 Comparison of **cac**’s and **cmc**’s for typical surfactant–polymer combinations.

Surfactant	Polymer	cac (mM)	cmc (nM)
C ₁₂ H ₂₅ —OSO ₃ [−] Na ⁺	PVP	2.5	8.3
C ₁₂ H ₂₅ —OSO ₃ [−] Na ⁺	POE	5.7	8.3
C ₁₀ H ₂₁ —OSO ₃ [−] Na ⁺	PVP	10	32
C ₁₂ H ₂₅ N(CH ₃) ₃ ⁺ Br ⁺	PAA [−] Na ⁺	0.03	16
C ₁₂ H ₂₅ N(CH ₃) ₃ ⁺ Br ⁺	Sodium alginate	0.4	16
C ₁₄ H ₂₉ N(CH ₃) ₃ ⁺ Br ⁺	PAA [−] Na ⁺	0.0025	3.8
C ₁₄ H ₂₉ N(CH ₃) ₃ ⁺ Br ⁺	Sodium alginate	0.03	3.8

PVP, polyvinylpyrrolidone; POE, polyoxyethylene; PAA[−]Na⁺, sodium polyacrylate.

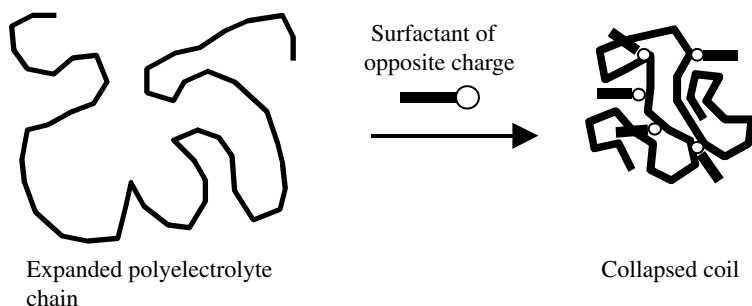


Figure 9.5 A schematic model for the interaction of charged polymer chains with surfactants of opposite charge (counter ions omitted for clarity).

interaction were not electrostatic, at least until all of the charge sites on the polymer chain are bound with surfactant molecules. In that case one can visualize a more complex structure that would involve an initial “coating” of charged sites along the chain through electrostatic interactions, producing a “hairy worm” complex. With the addition of more surfactant, hemimicelle seed regions might form that could then grow by the association of additional surfactant molecules through normal hydrophobic interactions. A hypothetical picture of such a process is given in Figure 9.5.

In the case of the interaction of sodium dodecyl sulfate (SDS) with the polar polymer POE, it is generally felt that the lower **cac** results from a stabilization of micelles by the adsorption of polymer onto the surface of the aggregate (Figure 9.6). The question is, does the micelle exist before polymer adsorption occurs, or does the polymer act as a seed for the aggregation process? Based on the observed acceleration of the aggregation process, it would seem logical to think that the polymer chain is an active participant in the process (seed) rather than just sitting around to adsorb onto a preformed aggregate.

A classical model for surfactant–polymer interaction is based on a stepwise sequence of binding between surfactant monomers (S) and the polymer chain (P), with each step being governed by the laws of mass action and with a unique rate constants, k_i , controlling each step:

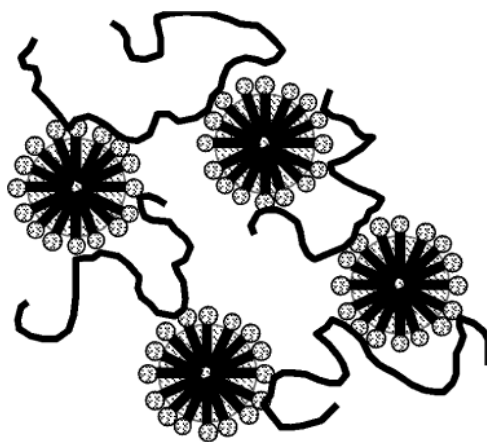
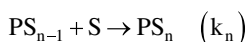
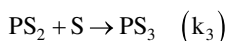
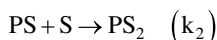
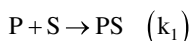


Figure 9.6 Schematic illustration of the effect of polymers on the aggregation of amphiphiles in solution.



The question of whether the sequential addition of surfactant molecules to the complex involves an addition to an aggregate unit or simply the adsorption of individual molecules followed by the aggregation process when the coil is "saturated" cannot be easily answered. In either case, a given polymer chain can only accommodate a limited number of surfactant molecules or aggregates. When the surfactant concentration exceeds the capacity of the polymer present to form the complex, additional surfactant appears to continue its "life as usual" until its normal **cmc** is reached. The values of the various surfactant-polymer interaction rate constants and their dependence on experimental conditions (e.g. temperature, solvent, ionic strength, pH) serve as a basis for formulating feasible descriptions of the molecular processes involved in the interactions. The combination of macroscopic and molecular information can provide valuable insight into the overall process.

In the above model, it is assumed that the stepwise binding process occurs initially through surfactant monomeric units. That is, there is no significant direct association of micelles or other aggregates with the polymer chain. The existence of such aggregate-polymer complexes is not excluded, however, since they may form on the chain as the total concentration of bound surfactant increases. It is only the stepwise association process that is limited to monomeric surfactant species. If polymer is added to a solution already containing micelles or other aggregate structures, a form of adsorption of polymer onto or into the aggregate cannot be ruled out. The nature of polymers in solution, especially the relatively slow kinetics of adsorption usually encountered, makes it difficult to say exactly what may be happening in the short term after mixing the two ingredients. That picture is also complicated by the differences of adsorption rates for polymer chains of different molecular weights. A smaller polymer chain will adsorb more rapidly, but it will also desorb more easily. A higher molecular weight chain will adsorb slowly but be very slow to desorb. The result is that a given system may exhibit certain solution characteristics (e.g. viscosity) that will change with time as the polymer chains and surfactant accommodate themselves to the most favorable energetic situation, that is, as thermodynamics overtakes kinetics.

Like all surfactant-related phenomena, surfactant-polymer interactions involve a complex balance of factors encouraging and retarding association and are understandable only if those factors can be reasonably estimated. The complications added by the energetics of polymer conformations in solution only add to the potential for confusion. The dominating forces can be broken down into the categories of electrostatic attractions and repulsions, dipolar interactions, including hydrogen bonding or acid-base chemistry, dispersion and van der Waals forces, and the overall hydrophobic effect. In most cases, combinations of those forces are involved, thereby adding to the fun of interpreting the experimental results. While the electrostatic processes are fairly straightforward, involving the interaction of charged species on the polymer with those on the surfactant molecule, the remaining interactions are less easily quantified and can be quite complex. Polymers in particular add their own new twists, since in solution they will have secondary and tertiary structures that may be altered during the binding process in order to accommodate the bound surfactant molecules. The nature of the surfactant-polymer complex may significantly alter the overall

energy of the system so that major changes in polymer chain conformation will result. Any and all of those changes may result in major alterations in the microscopic and macroscopic properties of the system.

Forces opposing the association of surfactant molecules with polymer chains include thermal energy, entropic considerations, solvent effects, and repulsive interactions among electrical charges of the same sign. It is clear that the strength and character of surfactant–polymer interactions depend on the properties of both components and the medium in which the interactions occur. However, even in systems where identical mechanisms are active for different surfactant and/or polymer types, the macroscopic symptoms of those interactions may be manifested in such a way that entirely different conclusions could easily be drawn.

As in the case of surfactants, four general types of polymer can be defined related to the electronic nature of the species: anionic, cationic, nonionic, and amphoteric. Not surprisingly, each polymer type will exhibit characteristic interactions with each surfactant class, with variations occurring within each group. It is little wonder, then, that surfactant–polymer interactions can produce some very “interesting” effects and become the subject of some lively discussions.

With the understanding that a great deal remains to be learned about the subject as a whole, the following comments will introduce a few of the observed facts about this field of study.

9.4.2 Nonionic Polymers

Probably the largest volume of published work in the field of surfactant–polymer interactions has involved surfactants and nonionic polymers such as polyvinylpyrrolidone (PVP), polyvinyl alcohol (PVA), polyvinyl acetate (PVAc), polypropylene glycol (PPG), methyl cellulose (MC), and polyethylene oxide (POE). The preferred surfactant has been (of course!) the classic – SDS. The results of most studies with SDS and similar surfactants indicate that the more hydrophobic the polymer, the greater the interaction with anionic surfactants. For a given anionic surfactant, it has been found that adsorption progresses in the order $PVP \geq PPG > PVAc > MC > PEG > PVA$. In such systems, the primary driving force for surfactant–polymer interaction will be van der Waals forces and the hydrophobic effect. Dipolar and acid–base interactions may be present, depending on the exact nature of the system. Ionic interactions will be minimal or nonexistent. For the polymer, it is reasonable to infer that the impact of the hydrophobic effect will be related to the ability of the polymer to undergo hydrogen bonding with the solvent (water), as well as the relative availability of nonpolar binding sites along the polymer chain.

If the primary mechanism of ionic surfactant/nonionic polymer interaction is hydrophobic, the adsorption of surfactant molecules will produce changes in the polymer chain conformation that are due to repulsions between the adsorbed ionic surfactant head groups (Figure 9.7). The properties of the solution will be altered as a result of such changes. For example, the solution viscosity may be found to increase substantially since the repulsion will force the polymer chain to uncoil or expand in the solution. If neutral salt is then added to such a system, repulsion between neighboring groups will be screened, and the expanded coil will contract or collapse, thus again affecting various macroscopic properties of the solution such as viscosity. Such expansion and collapse of surfactant–polymer complexes as a function of the extent of surfactant adsorption may be seen as being analogous to the solution behavior of polyelectrolytes as a function of the degree of dissociation and electrolyte content. In fact, the surfactant–polymer complex may be viewed as a non-covalent polyelectrolyte.

The bulk of the work on cationic surfactant/nonionic polymer interactions has utilized long-chain alkylammonium surfactants. It has been found that the interactions between such species

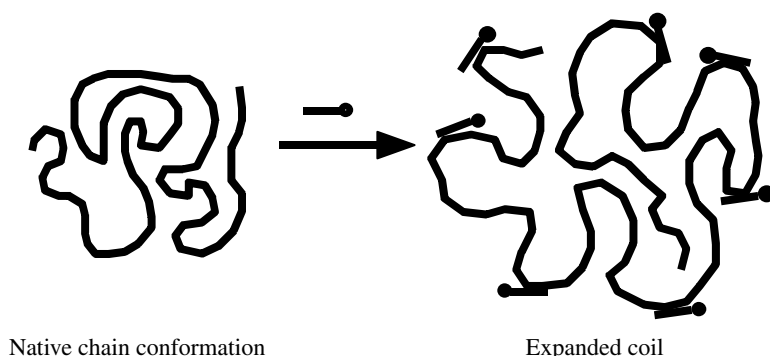


Figure 9.7 Schematic illustration of polymer coil expansion due to dispersion (hydrophobic) surfactant–polymer interaction.

become stronger as the chain length of the surfactant is increased, reflecting the greater drive to substitute surfactant–polymer for surfactant–water and polymer–water interactions. The nature of the cationic head group seems to have a significant effect on polymer–surfactant interactions. It has been found that the reduced viscosity of aqueous solutions of dodecylpyridinium thiocyanate/PVAc changed very little with variations in the surfactant concentration, whereas solutions of dodecylammonium thiocyanate/PVAc showed considerable viscosity increases with increasing surfactant concentration. Such a result might be interpreted as reflecting a reduced extent of surfactant adsorption onto the polymer chain due to the greater hydrophilicity of the pyridinium ring relative to that of the simple ammonium group. The relative binding strengths between nonionic polymers and cationic or anionic surfactants are difficult to compare. The general trends are that with a given polymer, anionics will exhibit stronger interactions than analogous cationic surfactants, all other things being equal.

The interactions between nonionic surfactants and nonionic polymers have been much less intensively studied than those for ionic surfactants. The limited number of reports available indicates that there is little evidence to indicate extensive direct surfactant–polymer association in such systems. Considering the size of the hydrophilic groups of most nonionic surfactants, their low **cmc**'s and the absence of significant possibilities for head group/polymer interactions, the apparent absence of substantial interactions is not conceptually hard to accept. An assertion that binding does not occur under any circumstance, however, would be foolish, given the complexities of polymer and surfactant science in general.

9.4.3 Ionic Polymers and Proteins

In many applications, it is more common for surfactants to encounter charged polymeric species rather than the nonionic examples discussed above. Practically all-natural polymers, including proteins, varieties of cellulose, gums, and resins, carry some degree of electrical charge. Many of the most widely used synthetic polymers such as polyacrylate ($\text{PAA}^- \text{M}^+$) and polymethacrylate ($\text{PMA}^- \text{M}^+$) salts do as well.

Polymers carrying electrical charges are usually termed “polyelectrolytes,” although the term may not always be applied to natural polymers or gums that have a small number of charges per chain. When one compares the possibilities for interactions between polyelectrolytes and surfactants with those for nonionic polymers, it is obvious that the presence of discrete electrical charges along the polymer backbone introduces the probability of significant coulombic interaction,

in addition to the nonionic factors mentioned previously. The polymers may be positively or negatively charged, or they may be amphoteric. The presence of charge on a polymer complicates the understanding of the solution properties of the polyelectrolytes. The potential for surfactant–polyelectrolyte interactions does so even more.

Polyelectrolytes, whether natural or synthetic, are of particular interest to surfactant users because of their application as viscosity enhancers (thickening agents), dispersing aids, stabilizers, gelling agents, membrane formers, binders, etc. They are also encountered in fibers and textiles and in natural surfaces and membranes in biological systems. Common synthetic polyelectrolytes include polyacrylic and methacrylic acids and their salts, cellulosic derivatives such as **CMC**, polypeptides such as poly-L-lysine, sulfonated polystyrenes and related strong acid-containing polymers, and polymeric polyammonium and imonium salts, and quaternized polyamines. Commonly encountered natural polyelectrolytes include cellulose, proteins, and various gums such as pectin, gum arabic, xanthan, locust bean, carrageenan, rosin acids, lignins, keratins, etc. In most cases, the charge on the polymer is fixed as either positive or negative, so possible interactions with surfactants of a given charge type can be reasonably well defined. While such factors as pH, electrolyte content, and the nature of the polymer counterion will affect the extent of interaction in given systems, the sense of the interaction (e.g. anion–anion, anion–cation, etc.) may not change significantly except where protonation or deprotonation of weak acids and bases occurs. Other polymers, proteins in particular, will be amphoteric in nature, the character of the net charge being determined by pH.

Not surprisingly, interactions between surfactants and polymers of similar charge are usually minimal, with electrostatic repulsion serving to inhibit the effectiveness of any non-electrostatic attractions. This is especially true for polymers having relatively high charge densities along the chain. That would be true for chains in which the charge distribution is relatively uniform. If the charges are, for some reason, clumped in specific regions of the chain, the door is left open for significant hydrophobic interaction in the unionized “bare” spaces along the chain.

When opposite charges are present, however, the expected high degree of electrostatic interaction is usually found to occur. In aqueous solution, the result of surfactant binding by electrostatic attraction is normally a reduction in the viscosity of the system; a loss of polymer solubility, at least to the point of charge reversal; and a reduction in the effective concentration of surfactant, as reflected by surface tension increases over what would be measured for that surfactant concentration in the absence of polymer.

Many naturally occurring random coil polyelectrolytes of a single charge type, including some carbohydrates, pectins, and keratins, are anionic and exhibit the same general surfactant interactions as their synthetic cousins. Proteins on the other hand are amphoteric polyelectrolytes, which possess a net charge character (anionic or cationic) that depends on the pH of the aqueous solution. Unlike most synthetic polyelectrolytes, natural polyelectrolytes such as proteins usually have well-defined secondary and tertiary structures in solution that can affect, and be affected by, surfactant binding. When secondary and tertiary structures are present, complications arise because of alterations to those structures during surfactant adsorption. The denaturation of proteins by surfactants is, of course, just such a process of the disruption of higher orders of structure in the dissolved polymer molecule.

The question of exactly how a surfactant interacts with a protein molecule has been the subject of a great deal of discussion over the years. In the case of interactions between bovine serum albumin (BSA) and SDS, the initial binding was found to involve the electrostatic association of oppositely charged species, especially at bound surfactant levels – i.e. the number of surfactant molecules low bound per polymer chain – of less than 10. As such binding occurs, the electronic character of the protein changes, possibly resulting in changes in its secondary and tertiary structure. Such changes may then lead to the exposure of previously inaccessible charge sites for further

electrostatic binding or of hydrophobic portions of the molecule previously protected from water contact by the secondary protein structure. Ultimately, as charge neutralization occurs, precipitation of the protein may result.

As the charges on a protein are neutralized by specific surfactant adsorption, association between the hydrophobic tail of the surfactant and similar areas on the polymer becomes more favorable, again changing the net electrical character of the polymer complex. At sufficiently high surfactant-protein ratios, reversal of the native charge of the protein will be the result, as illustrated in the lower portion of Figure 9.8. Macroscopically, the foregoing events may lead to dramatic changes in

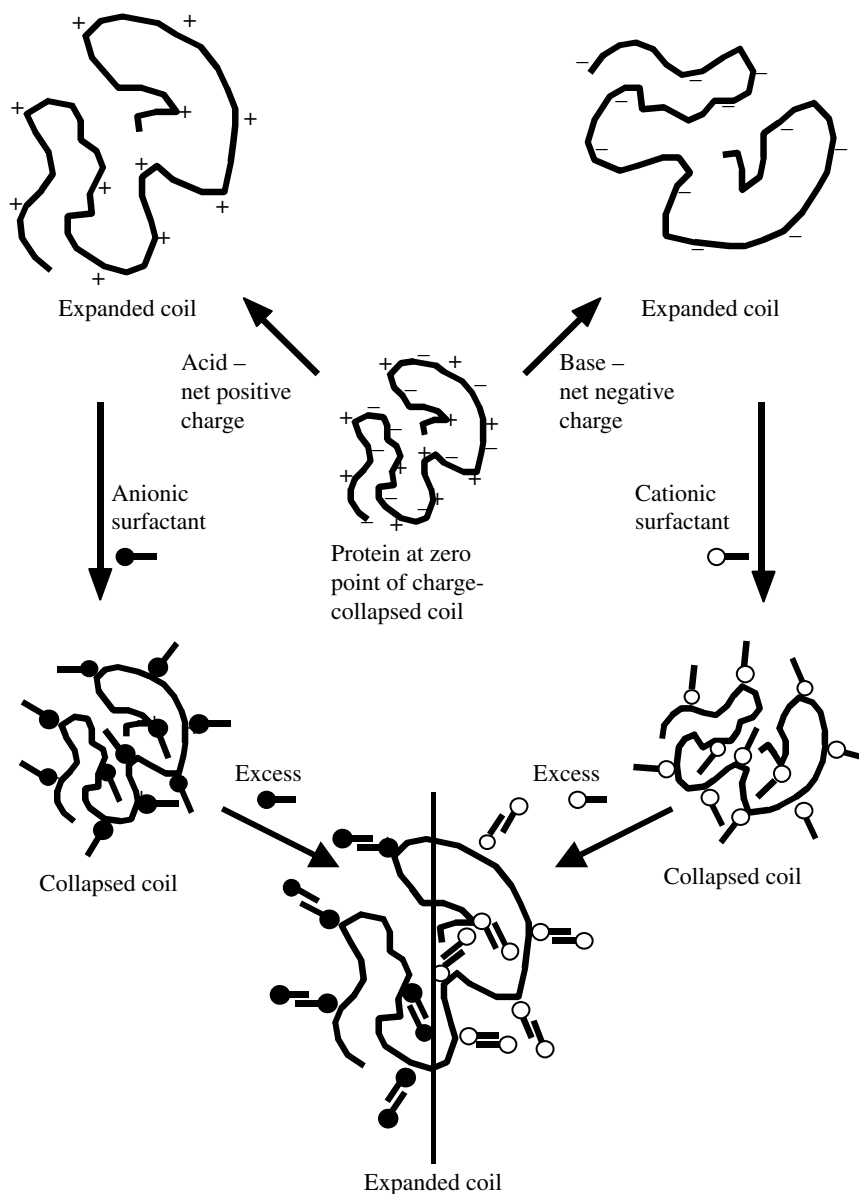


Figure 9.8 Representation of the collapse and charge reversal of proteins with change of pH and adsorption of surfactant of opposite charge.

the viscosity of the system as a result of, first, collapse of the polymer coil, followed by a rapid expansion after charge reversal has taken place. In addition, a minimum in the solubility of the polymer may be encountered, as evidenced by precipitation followed by reprecipitation. The effect is similar to that for proteins as the pH of the solution is changed, causing the polymer to pass through its zero point of charge (zpc) at which its water solubility is at a minimum.

When the bound surfactant level is high, exceeding approximately 20 surfactant molecules per chain, evidence supports the view that both the head group and the hydrophobic portion of the molecule become involved in the binding process. Behavior suggesting such complex formation has been found for deionized bone gelatin in the presence of several anionic surfactants. It was found that the extent of interaction as reflected by increases in the viscosity of the system was highly dependent upon the length of the hydrocarbon tail of the surfactant. For a series of sodium alkyl sulfates, the effect increased rapidly in the order $C_8 < C_{10} < C_{12} < C_{14}$.

The interactions between cationic and nonionic surfactants and proteins have received substantially less attention than the anionic case. Nonylphenol–POE nonionic surfactants undergo limited binding with proteins, although there is little evidence for sufficient interaction to induce the conformational changes found in the case of anionic materials. The limited number of results published on protein–cationic surfactant systems indicate that little cooperative association occurs in those systems, even if the native protein charge is negative.

Although it is clear that the surfactant binding processes are controlled by the same basic forces as the other solution and surface properties of surfactants, the location of binding sites on the polymer chain, the relative importance of the surfactant tail and head groups, and the exact role of the polymer structure remain to be more accurately defined. In any case, anyone proposing to use a surfactant in a formulation containing polymers, or in an application that entails surfactant–polymer interactions, must always consider the effect of each on the performance of the other.

More specific polymer–surfactant interactions can be obtained if the polymer chain is modified to introduce more hydrophobic groups along the chain. Such modifications provide more opportunity for hydrophobic interactions between the surfactant tail and the polymer. In addition, they may result in increased intra- and interchain polymer interactions, producing more compact chain conformations in aqueous solution or multichain polymer aggregates or micelles (Figure 9.9).

9.5 Polymers, Surfactants, and Solubilization

As discussed in Chapter 8, a useful characteristic of many micellar systems is their ability to solubilize water-insoluble materials such as hydrocarbons, dyes, flavors, and fragrances. Surfactant–polymer complexes, like polymeric surfactants, have been shown to solubilize materials at surfactant concentrations well below the **cmc** of the surfactant in the absence of polymer. The effectiveness of such complexes differs quantitatively from that of conventional micelles.

Studies have shown that the amounts of a hydrocarbon such as isooctane taken up by complexes of BSA and SDS depended linearly on the number of surfactant molecules bound to the protein molecule. They also showed that a minimum SDS cluster size of about 30 molecules bound to the BSA was required before any solubilization occurred. The solubilization isotherms for BSA/SDS also differed from those of SDS micelles alone. Those results indicate that, for the same isooctane activity, the BSA/SDS complexes had a greater solubilizing power than the micelles. In a similar way, it has been found that the addition of a polymer to a surfactant solution increased its solubilizing power, although no clear-cut correlations were established between the chemical structure of

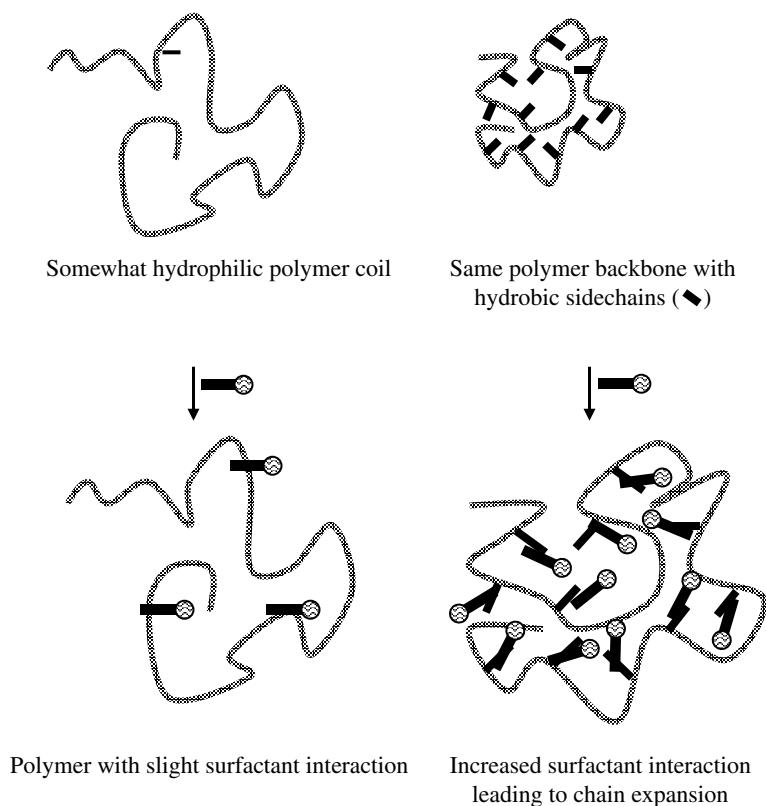


Figure 9.9 Possible solution effects of hydrophobic substitution on polymer chains and their potential effects on polymer–surfactant interactions.

the polymer and its effect on solubilization. In general, larger effects are observed for aromatic than aliphatic materials. The present state of knowledge in this area is not sufficient to allow quantitative predictions to be made about the solubilizing properties of surfactant–polymer complexes based solely on chemical composition, although it is known that their effectiveness depends on the nature of the polymeric component and the polymer/surfactant ratio.

9.6 Surfactant–Polymer Interactions in Emulsion Polymerization

Surfactant/polymer systems have additional technological significance since surfactants are normally used in the emulsion polymerization of many materials, often involving the solubilization of monomer in micelles prior to polymerization and particle formation. Surfactants have also been shown to increase the solubility of some polymers in aqueous solution. The combined actions of the surfactant as a locus for latex particle formation (the micelle) in some cases, particle stabilization by adsorbed surfactant, and as a solubilizer for monomer permit us to expect quite complex relationships between the nature of the surfactant and that of the resulting latex.

Within a given surfactant class, it is usually found that materials with high **cmc**'s produce latexes with larger particle sizes and broader size distributions. For example, the particle sizes of polyethylacrylate latexes prepared with sodium alkylsulfates ranged from 500 nm for the octyl to 50 nm for

the dodecyl surfactant. No similar trend was found for nonionic POE surfactants as a function of POE chain length.

The ability of surfactants to form complexes with polymer chains may also affect the ultimate properties and stability of the resulting polymer, especially when the macromolecule exhibits some affinity for or reactivity with water. Perhaps the best documented case of the effect of surfactant on latex stability is that of PVAc. The stability of PVAc latexes has been found to vary significantly depending on the surfactant employed in its preparation. It has also been found that PVAc could be dissolved in concentrated aqueous solutions of SDS and that it did not precipitate on dilution. The results suggest that, in this case at least, solubilization did not occur in the micelle but that extensive adsorption of surfactant onto the polymer chain was required. They also indicate that a strong, stable PVAc-SDS complex is formed that produces a water-soluble structure that is essentially irreversible, unlike normal micelle formation. Cationic and nonionic surfactants had little or no solubilizing effect under identical conditions, indicating the specific nature of many, if not most, polymer–surfactant interactions.

PVAc is, of course, the precursor for the preparation of PVA. The fact that surfactants such as SDS can promote the solubilization of PVAc has been used to explain the observed increase in the rate of hydrolysis of PVAc polymers prepared with that surfactant relative to materials prepared with a less strongly interacting POE–sulfate surfactant. The hypothesis is that the SDS adsorbs onto and solubilizes the polymer surface leading to a partial swelling of the particles, giving greater exposure to the hydrolytic environment, and loss of surfactant available for particle stabilization. As the surface of the PVAc particle is “eaten away” by the solubilization/hydrolysis process, the interior material becomes more exposed and subject to hydrolysis. The non-solubilizing surfactants, on the other hand, would not facilitate the hydrolysis process, reducing the rate of PVAc exposure to reactants in the aqueous phase. They would also remain adsorbed at the particle surface and continue to perform their function as stabilizers.

In polymers that have very little affinity for water, such as for polystyrene or alkyl acrylates and methacrylates, little effect of surfactant on water solubility would be expected. The action of surfactants in such latex systems would be limited to their action as monomer solubilizers during preparation and as adsorbed stabilizers afterward.

The complex relationships that can develop between polymers and surfactants add a great many question marks to the interpretation of data obtained from such systems. They also open the door to possible new and novel applications of such combinations, however, and will no doubt provide many interesting hours of experimentation and thought for graduate students and industrial researchers in the future.

10

Emulsions

As has been pointed out repeatedly, one of the most significant results of the physical phenomenon of “surface activity” is the preferential adsorption of amphiphilic molecules at interfaces, resulting in potentially dramatic changes in the characteristics of those interfaces. The ability to reproducibly control such adsorption and interfacial modifications is of immeasurable technological importance, not to mention the fact that our very existence as living organisms would be impossible had such a phenomenon not been a direct consequence of natural laws as we understand them. This chapter is concerned with one of the most important overall areas of impact of surfactants on our technological existence – emulsion formation and stabilization.

The preparation, stabilization, and use of systems of one fluid dispersed in a second, immiscible phase impact almost every aspect of our lives, from the food we eat to the pharmaceutical formulations that make our lives longer and more comfortable. As is always the case in any discussion of surfactants and their applications, definitions and nomenclature can play a significant role in the way the material is presented. Although by some definitions “foams,” dispersions of a vapor in a liquid or solid, could logically be considered to be a subclass of the general class of “emulsions,” the nature of such systems and the requirements for their preparation and stabilization make them sufficiently different from liquid–liquid systems to warrant their discussion in a separate chapter. For present purposes, we follow the definition that an emulsion is a heterogeneous system, consisting of at least one immiscible liquid dispersed in another in the form of small droplets, usually with a diameter of less than 0.1 mm. Such systems possess a minimal stability, which may be enhanced by the addition of amphiphilic materials, polymers or finely divided solids. Obviously, such a definition excludes foams and solid particulate dispersions from classification as emulsions, although it is possible that systems prepared as emulsions may, at some subsequent time, become dispersions of solid particles or foams.

When discussing emulsions, it is always necessary to specify the physical condition of each of the immiscible phases of the system. Since in almost all cases, at least one liquid will be water or an aqueous solution, it is common practice to describe an emulsion as being either oil in water (O/W) or water in oil (W/O), where the first phase mentioned represents the dispersed phase and the second the continuous phase. Although oil-in-oil (O/O) emulsions are not impossible, they are not commonly found. The generally high miscibility of most organic liquids is, of course, one limitation to the availability of such systems. More important, however, is the fact that few materials are sufficiently surface active at such O/O interfaces to impart the minimal stability necessary for their preparation and maintenance.

O/O emulsions do constitute an intermediate step in the preparation of nonaqueous emulsion polymers, although their existence as such is transient. Block polymers and comb polymers probably represent the most fertile area for research into emulsifiers and stabilizers for the preparation of O/O emulsions. They have so far found more application as stabilizers for dispersions of solids in organic solvents.

Before discussing the role of surfactants and their chemical structure in the preparation and stabilization of emulsions, it is important to have in mind a clear concept of the physical and theoretical aspects of liquid–liquid interfaces and the stabilization mechanisms available. Detailed discussions of these topics can be found in the works cited in the Bibliography. What follows is only a brief summary of some current thinking on the subject; no attempt is made to provide a comprehensive overview.

10.1 The Liquid–Liquid Interface

As discussed in Chapter 5, the presence of an interface induces an imbalance of forces that alters the energetic situation of molecules at or near that interface, usually giving molecules in that region a higher net energy than those in the bulk. The drive to lower the energy of the system resulting from the presence of the interface is one factor that results in the preferential adsorption of materials such as surfactants at such interfaces. The action of the adsorbed materials in lowering the free energy of the two-phase system reduces the work required to generate new interfacial area and therefore facilitates the preparation of emulsified systems.

The preparation of an emulsion requires the formation of a very large amount of interfacial area between two immiscible phases. If, for example, a sample of 10 mL of an oil is emulsified in water to give a droplet diameter of 0.2 mm, the resulting O/W interfacial area will have been increased by a factor of approximately 10^6 . The work required to generate one square centimeter of new interface is given by

$$W = \sigma_i \Delta A \quad (10.1)$$

where σ_i is the interfacial tension between the two liquid phases and ΔA is the change in interfacial area. If the interfacial tension between the oil and water is assumed to be 52 mN/m (as for a hydrocarbon liquid), the reversible work required to carry out the dispersion process will be on the order of 20 J. Since that amount of work remains in the systems as potential energy, the system will obviously be thermodynamically unstable and will rapidly undergo whatever transformations are possible to attain a minimum in potential energy (i.e. minimum interfacial area), including coalescence, creaming, and sedimentation. If some material can be added to the system that reduces the value of σ_i to approximately 1 mN/m, the magnitude of W will be reduced to 0.3 J – a substantial reduction in W , but still a thermodynamically unfavorable situation. Only if the interfacial tension (and therefore W) is zero can a truly stable system be obtained. Luckily, although thermodynamics will be the factor controlling the long-term stability of such an emulsion, kinetics can play a dominant role over the short term, and it is through kinetic pathways that most useful emulsions achieve their needed stability. It is clear, then, that while lowering the interfacial tension between phases is an important factor in the formation and stabilization of emulsions, it may not always represent the most important role of surfactants and emulsifiers in such systems.

The relationship between the adsorption of a molecule at an oil–water interface and the resulting interfacial tension is an important one and is briefly restated here. The Gibbs equation for a

system composed of one phase containing a nonionic solute adsorbing at the interface with a second phase is written as follows:

$$\Gamma_i = -\left(1/RT\right)\left(\delta\sigma_i/\delta\ln a_i\right)_T \quad (10.2)$$

where Γ_i is the surface excess of component i at the interface, σ_i is the interfacial tension between the two liquid phases, and a_i is the activity of component i in the system. The equation shows that at a liquid–liquid interface, the amount of surfactant adsorbed can be determined from the slope of the curve of σ_i versus $\ln a_i$. In dilute surfactant systems, the concentration c_i (mol/L) can be substituted for activity without serious loss of accuracy. The simple relationship of the Gibbs equation can have significant practical application in the preparation of emulsions, especially in defining the relationship between emulsion droplet size and total surfactant concentration.

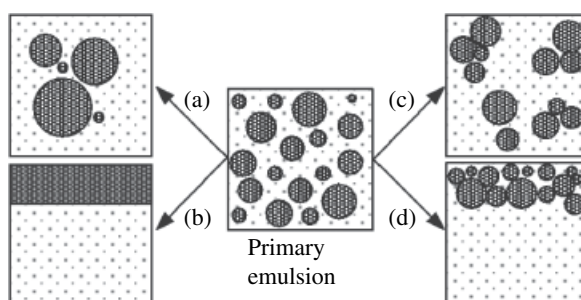
10.2 General Considerations of Emulsion Stability

Even though emulsions as defined above have been in use for thousands of years (even longer if natural emulsions are considered), no comprehensive theory of emulsion formation and stabilization has yet been developed that quantitatively describes, and predicts, the characteristics of many of the complex emulsions and formulations that may be encountered while working in this field. Except in very limited and specialized areas, the accurate prediction of such aspects of emulsion technology as droplet size and distribution and stability remains more in the realm of art than science.

To serve as a complete theoretical description of emulsions, a theory must be able to explain and predict all aspects of emulsion formation, stability, and type (O/W or W/O), the influence of environmental factors such as temperature and pressure, the role of emulsifiers and stabilizers and their chemical structures, the role of the chemical structures of the immiscible phases, and the effects of additives in each phase. That represents a very tall order, as illustrated by the fact that even though vast amounts of experimental data relating to each of those questions are available, no generally applicable theory has yet appeared.

When discussing the stability of an emulsified system, it is important to have a clear idea of the physical condition of the components and the terminology employed. Four terms commonly encountered in emulsion science and technology related to stability are “breaking,” “coalescence,” “creaming,” and “flocculation.” Although they are sometimes used almost interchangeably, those terms are in fact quite distinct in meaning as far as the condition of an emulsion is concerned. Coalescence, for example, refers to the joining of two (or more) drops to form a single drop of greater volume, but smaller interfacial area (Figure 10.1a). Such a process is obviously energetically

Figure 10.1 The ultimate fates of emulsions related to colloidal stability: (a) coalescence, (b) breaking, (c) flocculation, and (d) creaming.



favorable in almost all cases. Although coalescence will result in significant microscopic changes in the condition of the dispersed phase, such as changes in average particle size and distribution, it may not immediately result in a macroscopically apparent alteration of the system. The breaking of an emulsion (Figure 10.1b) refers to a process in which a gross separation of the two phases occurs. The process is a macroscopically apparent consequence of the microscopic process of drop coalescence. In such an event, the identity of individual drops is lost, along with the physical and chemical properties of the emulsion. Such a process obviously represents a true loss in the stability of the emulsion.

Flocculation refers to the mutual attachment of individual emulsion drops to form flocs or loose assemblies of particles in which the identity of each is maintained (Figure 10.1c), a condition that clearly differentiates it from the action of coalescence. Flocculation can be, in many cases, a reversible process, overcome by the input of much less energy than was required in the original emulsification process. Finally, creaming is related to flocculation in that it occurs without the loss of individual drop identities (Figure 10.1d). It will occur over time with almost all emulsion systems in which there is a difference in the density of the two phases. The rate of creaming will depend on the physical characteristics of the system, especially the viscosity of the continuous phase and the density difference between the two phases. It does not necessarily represent a change in the dispersed state of the system, however, and often it can be reversed with minimal energy input. Obviously, both flocculation and creaming represent conditions in which drops “touch” but do not combine to form a single unit. The key to understanding the true stability of emulsions, then, lies on the line separating the processes of flocculation and coalescence.

Even in the infancy of emulsion technology several thousand years ago, it was recognized that to obtain a useful emulsion with any long-term stability, it was necessary to include a third component, at least, that served some “magical” purpose and imparted the required degree of stability. Such additives included simple inorganic electrolytes; natural resins and other macromolecular compounds; finely divided, insoluble solid particles that located themselves at the interface between the two phases; and amphiphilic or surface-active materials that were soluble in one or both phases and significantly altered the interfacial characteristics of the system. Although the focus of this chapter is the role of surface-active, monomeric materials in emulsion preparation and stabilization, it may be of interest to briefly discuss some aspects of the influence of the three other stabilizing classes since, in practice, combinations are most often employed. The four mechanisms are illustrated schematically in Figure 10.2.

The least effective additives for the enhancement of emulsion stability are the inorganic electrolytes. Materials such as potassium thiocyanate (KCNS), when included in an emulsion formulation at the proper levels, may facilitate the preparation of dilute O/W emulsions. The stability of such emulsions, while greater than that of the system in the absence of the electrolyte, will be very limited. It is generally assumed that such action by simple electrolytes stems from the limited adsorption of the anionic species at the oil–water interface, imparting a weak electrical double layer that retards the close approach, and thus coalescence, of individual drops in the emulsion. Because the adsorption of such ions at the interface is small, the electrical effect is slight and provides only limited, short-term resistance to the breaking of the emulsion. Because of their limited utility and effectiveness, such materials are not included in the general classification of materials as emulsifying agents or emulsifiers. The remaining three classes of materials constitute what are referred to as true emulsifiers and stabilizers. By their strong preferential adsorption at the O/W interface, these materials provide a much greater interfacial effect than the simple electrolytes and make possible the extremely diverse technological applications of emulsions we see today.

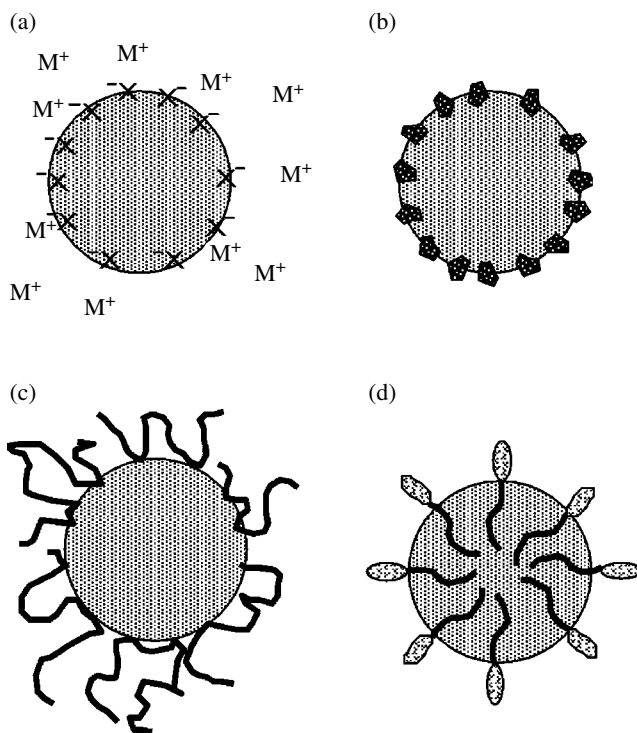


Figure 10.2 Mechanisms for the stabilization of emulsions: (a) specific ion adsorption, (b) solid particles, (c) the adsorption of polymer chains, and (d) amphiphile adsorption.

In nature as well as in man-made technology, macromolecular emulsifiers and stabilizers play a major role in the preparation and stabilization of emulsions. Natural materials such as proteins, starches, gums, and their modifications, as well as totally synthetic compounds such as polyvinyl alcohol, polyacrylic acid and other polyelectrolytes, and polyvinylpyrrolidone, have several characteristics that make them extremely useful in emulsion technology. By the proper choice of chemical composition, such materials can be made to adsorb strongly at the interface between the continuous and dispersed phases. By their presence, such materials can reduce the energetic driving force to coalescence by lowering the interfacial tension and/or forming a mechanical barrier between drops.

The effectiveness of polymeric materials at lowering interfacial tensions is often limited by their relatively slow rate of diffusion to the interface, but that is not always the case. More important to their function is the fact that polymers can form a substantial mechanical and thermodynamic barrier at the interface that retards the approach and coalescence of individual emulsion droplets. The polymeric nature of the materials means that each molecule can be strongly adsorbed at many sites on the interface. As a result, the probability of desorption or depletion is very small, and the interfacial layer attains a degree of strength and rigidity not easily found in systems of monomeric materials. In addition, the presence of polymeric materials in the system can retard processes such as creaming by increasing the viscosity of the continuous phase in addition to reducing the rate of droplet encounters, which could lead to flocculation or coalescence.

A second class of effective emulsifying agents commonly encountered consists of the finely divided solid particles. It has been known for some time that particles of colloidal dimensions

(<1 mm in diameter, for example) that are wetted by both aqueous and organic liquids can form stabilizing films and produce both O/W and W/O emulsions with significant stability. Emulsion stabilization by solid particles relies on the specific location of the particles at the interface to produce a strong, rigid barrier that prevents or inhibits the coalescence of drops. If the solid has a native electrical charge, it may also impart a degree of electrostatic repulsion that enhances the overall stabilizing power of the system.

There are three keys to the use of particulate solids as emulsion stabilizers: particle size, the state of stabilizer particle dispersion, and the relative wettability of the particles by each liquid component of the emulsion system. The stabilizer particles must be small compared with the emulsion droplet and in a state of incipient flocculation. That is, the particle dispersion must be near the limit of stability so that their location at the interface will result in some attractive particle–particle interaction to give strength to the system.

For the third condition, the solid must exhibit a significant contact angle at the three-phase (oil/water/solid) contact line, as measured conventionally through the aqueous phase. For maximum efficiency, it is usually found that the stabilizer should be preferentially wetted by the continuous phase. If the solid particles are too strongly wetted by either of the two liquid phases, the optimum stabilizing action will not be attained. It is usually necessary, therefore, to closely control such factors by controlling the system pH or by adding materials that adsorb onto the particles and impart the required surface characteristics. For example, if a mineral particle is used, but it is wetted too well by the aqueous phase, it can be treated with amphiphilic materials that will partially or completely coat the particle surface and thereby modify its interactions with water and/or the oil phase. A similar effect may, in some cases, be achieved by modifying the surface charge of the particles through specific ion adsorption, pH changes, adsorption, etc. More details on those processes are given in Chapter 12.

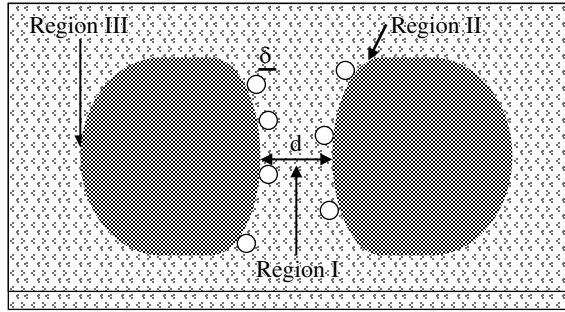
The last major class of emulsifiers and stabilizers is that of the monomeric surfactants that adsorb at interfaces and produce electrical, mechanical, and steric barriers to drop coalescence, in addition to their role in lowering the interfacial free energy between the dispersed and continuous phases. Since these materials are the central concern of this work, they are addressed in detail below.

10.2.1 The Lifetimes of Typical Emulsions

Any discussion of the stability of emulsions must be concerned not only with the mechanism of stabilization but also with the time frame of the stability requirements and the conditions of preparation. The rates of degradation of emulsions vary immensely, and it is not possible to define a single number that can be used as a measure of acceptable or unacceptable stability – that must be defined by end-use requirements. In any emulsion, especially one has no specific stabilization mechanism incorporated or one in which the stabilization is minimal, the degradation or breaking process will involve the coalescence of droplets brought together by Brownian motion, thermal convection currents, and random mechanical disturbances. Their stability can usually be measured on the order of seconds or minutes. In the presence of gentle agitation, the process may be accelerated, while more vigorous stirring may result in the occurrence of competitive processes of coalescence and new droplet formation. Therefore, moderate agitation may result in the development of a steady-state or equilibrium particle size distribution that will be highly dependent on the rate of agitation, the concentration of the dispersed phase, and the conditions of disturbance.

Emulsions that contain more effective stabilizing additives such as one of those described above may be stable for hours, days, or months. In such systems the action of random or induced motion

Figure 10.3 The deformation of emulsion droplets due to compaction during creaming or sedimentation stretches the stabilizing interfacial membrane and potentially reduces stability.



and droplet collision will continue, but the interfacial layers will possess sufficient strength and rigidity to prevent coalescence in most cases. When emulsion creaming (or sedimentation) occurs, additional pressures are applied to the interfacial area. At extreme pressures, as in the process of centrifugation, the drops may be deformed into the shape of polyhedra. In such a case, the interfacial area per unit volume will increase, and the stabilizing layer will be stretched, reducing its strength and possibly leading to rupture and breaking (Figure 10.3).

In addition to the mechanical actions and interfacial potential energy considerations that will act to reduce the degree of dispersion of an emulsion, other considerations act to limit their stability. One such factor affecting long-term stability is the phenomenon, commonly termed “Ostwald ripening” in crystalline systems, in which large drops (or crystals) are found to grow at the expense of smaller ones. Such action, whether in a crystalline or emulsion system, results from differences in the chemical potential (and therefore solubility) of molecules in small particles relative to those in larger ones. Such differences arise from the fact that the Laplace pressure, Δp , inside a drop is inversely proportional to the drop radius, r :

$$\Delta p = 2\sigma_i/r \quad (10.3)$$

In terms of the Kelvin equation and solubility, the effect of radius can be given as

$$\ln(S_1/S_2) = \sigma_i V/RT(1/r_1 - 1/r_2) \quad (10.4)$$

where S_1 and S_2 are the solubilities of the particles of radii r_1 and r_2 and V is the molar volume of the phase inside the droplets or crystals. The effect of the Kelvin relationship is often readily apparent in foam systems (Chapter 11), where the solubility of gases in the liquid phase can be substantial. In emulsion systems, on the other hand, the solubility of the dispersed phase may be so low that diffusion from small to large droplets will be exceedingly slow. The process will occur even in such circumstances, but at such a rate that it will not be apparent for long periods. In that context, it is often possible to greatly reduce the rate of droplet growth due to Laplace pressures by employing emulsifiers that form a barrier to the passage of dispersed phase molecules into the continuous phase. The presence of a large excess of surfactant in the form of micelles capable of solubilizing the dispersed phase could obviously be detrimental to long-term stability due to the enhancement of the Ostwald ripening effect.

Other external factors affecting the stability of emulsions include the actions of bacteria and other microorganisms that can degrade components and significantly alter the characteristics of the system, and freezing, especially in O/W emulsions. During the process of freezing, the formation of ice crystals in the continuous phase forces the emulsion droplets together under significant

pressures, often resulting in the rupture of the interfacial film and drop coalescence. It is obvious, then, that stability to such action will require an interfacial film of considerable strength. Even though the protection of emulsions from breaking due to freezing action is of considerable economic importance, there has been relatively little fundamental research published in the area.

Bacterial action can be of importance in food, pharmaceutical, and cosmetic emulsions. Such systems are obviously of great economic importance, and a great deal of research has been devoted to the problem. When biological stability is important, some advantages can be gained by the proper choice of surfactant in the stabilizing formulation, since many such materials show significant bacteriostatic activity.

From the discussion above, it is clear that, from a surface chemical point of view, one aspect of emulsion stability is of primary importance – the protection of the emulsion droplets from coalescence. As a result, that area has received the greatest overall amount of attention from both academic and industrial research efforts. Flocculation without coalescence, however, is an important consideration and has begun to draw closer and more frequent attention, especially concerning the role of polymeric species that may act as bridging agents between droplets. The physical characteristics of the interfacial film – its strength and rheological properties – are beginning to come under closer examination as new techniques for such studies become available. Several excellent reviews and monographs published in recent years cover in detail the questions raised above. Some of those are listed in the Bibliography.

10.2.2 Theories of Emulsion Stability

Early “practical” theories of emulsion stability recognized the importance of additives such as surfactants, polymers, and particulates to the processes of emulsion preparation, the type of emulsion produced, and the overall stability of the final system. However, a reasonably sound theoretical picture began to evolve once an understanding of the concepts and principles of interfaces and monolayers began to become clear. Studies of oriented amphiphilic monolayers at interfaces led to the conclusion that such structures, in which each portion of the adsorbed molecules showed a strong preference for association with one of the two liquid phases, offered the best explanation for observed experimental results. As a result, it became possible to schematically represent the emulsion droplet as shown in Figure 10.2d.

The concept of an adsorbed monolayer film acting as an emulsion droplet stabilizer found early experimental support in work showing that the equilibrium area per molecule of surfactant at an oil–water interface, as determined from final droplet diameters, approached a constant value, regardless of initial surfactant concentrations. That is, the area occupied by adsorbed amphiphilic molecules, initially carboxylate soaps, had a lower limit related to the nature of the molecule. It was found that emulsions in which the level of surfactant at the oil–water interface corresponded to an “expanded” monomolecular film were much less stable than those in which sufficient stabilizer was present for the formation of a “condensed” film. For purposes of the present discussion, an expanded monomolecular film may be roughly defined as one that has a relatively high compressibility compared with the bulk liquid but exists as a continuous interfacial monolayer (Figure 10.4a); that is, it has the basic characteristics of a compressible gas, rather than being a collection of isolated “islands” of amphiphilic molecules (Figure 10.4b). The “condensed” film, on the other hand, will have relatively low compressibility, existing as a close-packed monomolecular array (Figure 10.4c).

Similar studies explored the role of film tenacity in emulsion stabilization. Such studies compared the stability of emulsions prepared with mixtures of surfactants to the ability of monomolecular

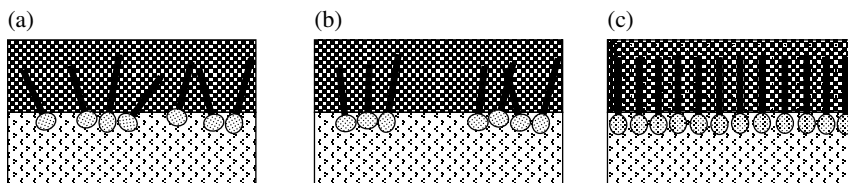


Figure 10.4 A schematic representation of adsorbed surfactant monolayers: (a) a compressible monolayer film, (b) hypothetical "islands" of amphiphile, and (c) a condensed monolayer.

films of the same compositions at the air–water interface to resist high surface pressures without film breakdown. The results indicated that the more resistant the film to high surface pressures, the greater the stability of the related emulsion. It was clear to investigators some time ago, therefore, that the nature of the interfacial film stabilizing an emulsion played an important role in determining the ultimate stability of the dispersed system. To this day, however, there is still some question as to some of the exact details of the stabilization process.

The effectiveness of any adsorbed film of amphiphilic materials in retarding the inevitable movement of emulsified systems toward a minimum in total energy may be considered in at least three contexts. The adsorbed molecules can (i) reduce the potential energy of the dispersed system by lowering the interfacial tension; (ii) erect a rigid or highly viscous barrier at the interface capable of preventing or retarding the coalescence of droplets that collide as a result of random Brownian motion, thermal convection, or mechanical agitation; and (iii) in cases where the adsorbed molecules carry an electric charge, impart that charge to the surface of droplets, resulting in the formation of an electrical double layer that lessens the frequency and effectiveness of close droplet approach and contact leading to droplet growth.

Although it may be tempting to attribute emulsion stability to the existence of a low interfacial tension, Eq. (10.1) shows that even a low value of σ_i will still result in a relatively high value for the work required for the formation of fresh interface. It is generally felt today that interfacial tension effects are less important to overall long-term emulsion stability than the effects of the nature of the interfacial film. The ability of the interfacial film to withstand the pressures of droplet contacts (its tenacity), its properties as a barrier to the passage of dispersed phase into the continuous phase (to limit Ostwald ripening), and its ability to erect a steric or electrical barrier to droplet approach and contact appear to be the major characteristics determining the ultimate stability of an emulsion. With those concepts in mind, we now turn more specifically to the role of surfactants in the preparation and stabilization of emulsions.

10.3 Emulsion Type and the Nature of the Surfactant

The concept that surfactant molecules preferentially orient at the oil–water interface not only clarified the picture of monomolecular film stabilization but also shed light on the problem of explaining the emulsion type obtained as a function of the chemical structure of the adsorbed species. It was recognized early that the nature of the surfactant employed in the preparation of an emulsion could control the type of emulsion formed. It was found, for example, that while the alkali metal salts of fatty acid soaps produced O/W emulsions, the use of di- and trivalent soaps resulted in the formation of W/O systems. The adsorbed monolayer mechanism for the stabilization of emulsion droplets requires the formation of a relatively close-packed surfactant film at the interface. It is clear that the geometry of the adsorbed molecules must play an important role in the effect

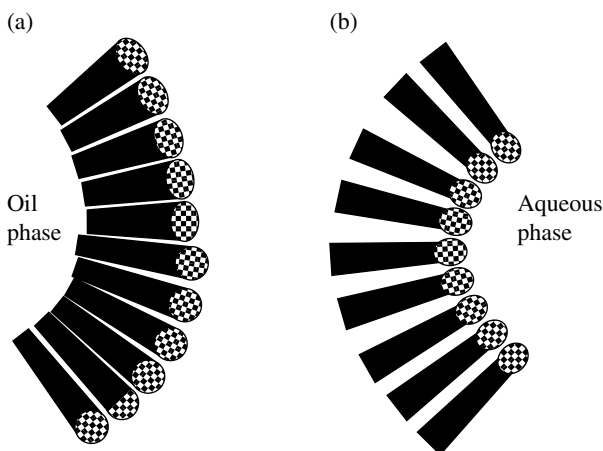


Figure 10.5 A schematic representation of the “oriented wedge” picture of emulsion stabilization by adsorbed surfactant monolayers: (a) wedge favoring O/W emulsions and (b) W/O systems.

obtained. For efficiency of packing, it can be seen from Figure 10.5 that the formation of W/O systems with polyvalent soaps is almost inevitable, since they can be seen as double-tailed surfactants, while the monovalent analogues are single tailed. Such a steric requirement in terms of the orientation of surfactant molecules at the interface has classically been referred to as the “oriented wedge” theory. Such a concept has now been given theoretical validity by the molecular geometry and critical packing parameter concepts discussed particularly in Section 6.4.

Although such a simple view of the role of the monolayer in determining the nature of the emulsion can be quite useful, exceptions are known. Such exceptions probably reflect the conflicting role of solubility in stabilization, since some monovalent salts with relatively low water solubility produce W/O emulsions. A rule of thumb for predicting the type of emulsion formed based on the relative solubility of the surfactant employed, often referred to as the Bancroft rule, states that the liquid in which the surfactant was most soluble would form the external or continuous phase. The rule was extended by the assertion that the presence of an absorbed interfacial film required the existence of two interfacial tensions: one at the oil–monolayer interface and a second at the water–monolayer interface. Since the two tensions would not, except in very unusual circumstances, be equal, the interfacial layer would be curved, with the direction of curvature determined by the relative magnitudes of the two tensions. Logically, the film will curve in the direction of the higher interfacial tension so that the phase associated with that interface will become the dispersed phase in the system (Figure 10.5).

Aside from the nature of the emulsifier employed, the relative amounts of the two phases in the system might be expected to affect the type of emulsion obtained. If one assumes that an emulsion is composed of more or less rigid, spherical droplets of equal size (highly unlikely in reality), simple geometry shows that the maximum volume fraction of dispersed phase that can be obtained is approximately 74%. It was suggested that any emulsified system in which that level was exceeded would produce less stable, deformed droplets and would lead to phase inversion to an emulsion of the opposite type. Practice has shown, however, that it is possible to prepare emulsions of dispersed phase volume fractions far exceeding that theoretical limit. Seen with the (sometimes) 20/20 vision of hindsight, there are several possible ways to explain the failure of such a simple geometric approach.

In the first place, emulsion droplets are not and can likely never be perfectly monodisperse; as a result, it is possible for smaller droplets to insert themselves in the void spaces between close-packed, larger droplets (Figure 10.6), increasing the total potential packing density of the system. In addition, emulsion droplets are not rigid spheres, but highly deformable; thus, they can be easily

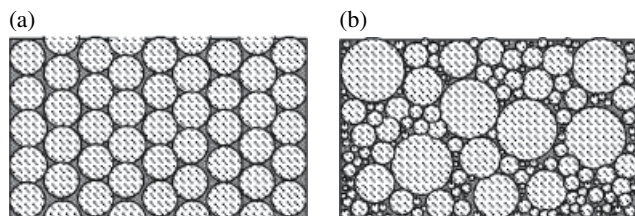


Figure 10.6 The effect of droplet polydispersity on the potential packing density of emulsions; interstitial spaces between larger drops may be filled by smaller units: (a) ideal hexagonal close packing and (b) high density polydisperse packing.

deformed from spherical to various oval or polyhedral shapes to fit the demands of the system. Large excursions from a spherical shape are, of course, generally unfavorable, since they entail the formation of additional interfacial area for a given dispersed volume fraction. As mentioned above, such an increase in interfacial area could strain the ability of the adsorbed emulsifier film to the point of droplet coalescence.

In the past there have been some suggestions that the mechanical process of emulsification could also play a role in determining the type of emulsion produced. A number of studies have verified that, in some cases at least, such a mechanical effect on emulsion characteristics does seem to exist for some specific formulations.

A fully satisfying theoretical explanation for such an effect, however, has not been worked out. It is found, however, that the order and manner of mixing the components of the two phases can significantly affect the quality and stability of the resulting emulsion. Some cosmetic formulations, for example, give better results if the aqueous phase is added to the organic phase rather than the reverse, even though the final emulsion is of the O/W type. Possible mechanical and procedural questions aside, most theories of emulsion formation place the most emphasis on the natures of the continuous and dispersed phases and the nature of the emulsifying agent employed.

10.4 Surface Activity and Emulsion Stability

To be a generally applicable description of emulsions, a theory must not only explain and predict the consequences of the system composition and conditions of preparation on emulsion type, but it must also be able to accurately relate the long-term stability of the system to all those factors. Even in the light of the vast amounts of experimental data on emulsions published to date, no generally applicable theory has been developed that can handle all modern emulsion formulations. That should not be taken as a mark against the science, however, since a glance at the list of ingredients for most modern emulsions may be as long as your arm! With so many actors on the stage, the theory may become as complex as the precise calculation of all of the gravitational interactions of all of the planets and satellites in our solar system.

Modern attempts to formulate a quantitative theory of emulsions and emulsion stability have looked most closely at the nature of the interfacial region separating the two immiscible phases, especially the chemical and physical nature of the adsorbed film, the role of mixed films and complex formation, interfacial rheology, and steric and electronic factors at the interface. The theoretical foundations for current ideas concerning emulsion formation and stability are presented in several of the references cited in the Bibliography. A few of the most basic ideas, however, are presented below.

In order to picture what is happening when two emulsion droplets undergo close approach, one can think of two water-filled balloons being pushed together. As they begin to interact, the approaching surfaces begin to deform or flatten. Air between the balloons is also forced out of the interstitial region. The membranes separating the contents of the balloons will be stretched, but their strength is (usually) sufficient so that rupture does not occur. As indicated in Figure 10.3, a similar deformation occurs as two emulsion droplets undergo close approach, except that the interfacial membranes involved do not have the same physical strength as the balloons. So other mechanisms must act to prevent a complete coalescence of the drops.

As the emulsion droplets approach during the process of flocculation or coalescence, a thin lamellar or interstitial film of the continuous phase will form between them (Figure 10.7b). When the film begins to reach a critical thickness, solvent and counterions associated with the adsorbed surfactant molecules begin to be squeezed out (Figure 10.7c). If the surfactant in the monolayer is not strongly adsorbed, it may desorb, and its interfacial concentration may become depleted significantly reducing its stabilizing effectiveness to such an extent that drop coalescence occurs. If the adsorption is sufficiently strong, osmotic forces will try to bring the counterions and associated solvent back into the interstitial region, forcing the drops apart and maintaining the stability of the emulsion. In the case of flocculation, there may be an optimum separation distance at which the forces of attraction between drops and the osmotic forces and electrostatic repulsion are balanced and the drops remain closely associated without coalescence.

If rupture and coalescence take place (Figure 10.7d), it occurs in an area of the adsorbed monolayer thinned out by the mechanical action of the approaching drops in stretching the monolayer as a result of deformation and increases in the interfacial area and/or of depletion of emulsifier due to desorption. Understanding the behavior of such lamellar films and the role of surfactants in their action requires an understanding of the forces involved in interactions across the film and the kinetic aspects of film fluctuations.

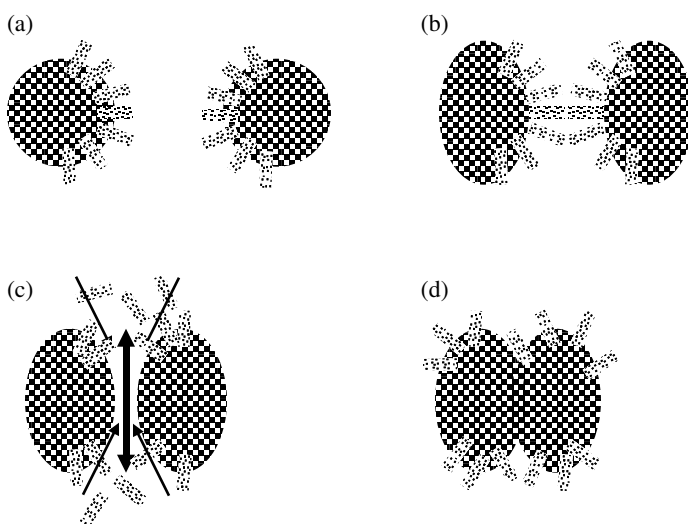
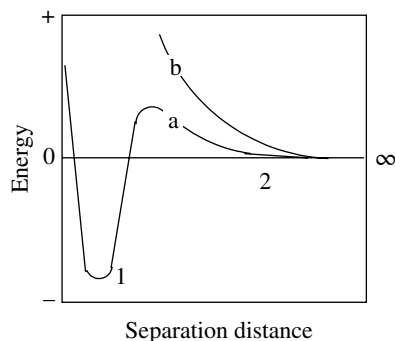


Figure 10.7 A schematic representation of the mechanisms leading to the weakening of adsorbed monolayers and the possible coalescence of the drops: (a) isolated emulsion drops, (b) as drops undergo close, deformation begins, (c) surfactant forced out (heavy arrow) as osmotic forces try to re-establish the stabilizing layer (light arrows), and (d) membrane rupture and drop coalescence.

Figure 10.8 Representative potential energy diagrams: (a) electrostatic stabilization with primary (1) and sometimes secondary (2) minima and (b) steric stabilization.



The coalescence of liquid droplets, therefore, is intimately related to the nature of the thin lamellar film formed between them as they are brought into close encounters as a result of thermal convection, Brownian motion, or mechanical agitation. It is important to understand the nature of the forces acting across the film in order to have information about the thermodynamic stability, metastability, or instability of the film and the kinetic processes that will control the rate of film breakdown. Comprehensive reviews of those aspects of emulsion stability can be found in the comprehensive works edited by Becher and references cited therein.

When two liquid droplets possessing adsorbed monomolecular stabilizing films come into close proximity on a colloidal scale (Figure 10.8), the thin film region will develop in the area of closest approach, forming two essentially flat, parallel monolayers separated by a distance d (region 1), a transition region at the ends of the parallel layers where the surface curvature is large relative to that of unaffected droplets (region 2), and regions well away from the lamellar region where curvature is that of the undeformed interface (region 3).

When discussing the forces acting across the lamellar film, it is necessary to consider two ranges for the value of the separation distance d : (i) that in which d is greater than twice the thickness of the monomolecular films d_m ($d > 2d_m$) and (ii) that in which d is less than $2d_m$. In the first case, the significant forces are those considered to be long range in the colloidal sense: van der Waals and electrical double-layer interactions. Such interactions can be characterized by conventional potential energy diagrams (Figure 10.8), which relate the potential energy of interaction of the two drops to their distance of separation. The shape of the diagram will be a function of the nature of the attractive and repulsive forces acting between the approaching drops. In Figure 10.8a, the combination of attractive van der Waals and repulsive electrostatic forces will normally show the presence of a maximum and primary and secondary minimum as a function of the distance of separation. In general, the secondary minimum, when present, will represent a state of reversible flocculation. The primary minimum, on the other hand, represents a state of irreversible coalescence.

If the lamellar film between approaching emulsion droplets thins beyond $d > 2\delta$ (Figure 10.3), with no drop coalescence taking place, interactions generally referred to as steric repulsions come into play (Figure 10.8a). Such repulsions normally result in a steep maximum in the potential energy curve. Interfacial film rupture, then, requires that those repulsive forces be overcome by deformation of the interfacial film of adsorbed surfactant or emulsifier. The so-called steric or enthalpic stabilization mechanism will generally produce a monotonic curve of increasing potential energy (Figure 10.8b). Conceptually, that process may be visualized as arising because the space between the stabilizing layers is reduced to such an extent that the two layers become compacted and further compression becomes more difficult. If the components of those layers were

rigidly fixed and unable to move, there should develop an essentially infinite barrier to drop coalescence. In some colloidal systems, particularly solid particles having adsorbed polymeric stabilizing layers, such a mechanism can often provide much greater stability than electrostatic forces. In emulsion systems employing normal surfactants, the effectiveness of steric stabilization process is limited by the fluidity and deformability of the dispersed phase, as well as by the fact that monomeric surfactant layers are not generally rigid. Adsorbed molecules may move around relatively freely, especially under the influence of the forces developed during drop approach. As will be seen in later sections, situations do arise in which emulsion stability can be enhanced by the presence of less fluid interfacial structures such as molecular complexes and liquid crystals. In the present context, we are interested only in the specific roles that surfactants can play in affecting film drainage and rupture.

The presence of almost any surface-active species will result in an increase in the stability of most oil–water systems subjected to agitation, as is often painfully obvious to any organic chemist attempting to purify a reaction product by solvent extraction. The action of many organic materials, even those not normally considered to be surfactants, in lowering the interfacial tension between the water and oil phases affects both the ease with which the interfacial area can be increased and the rate at which individual droplets will coalesce and lead to complete phase separation.

The exact role of interfacial forces in emulsion stabilization is the subject of some question. In the view of many researchers in the field of emulsion stabilization, the rate of failure of the adsorbed lamellar film at the droplet interfaces as they approach, and touch is a primary factor in the stabilization of an emulsion system. Such phenomena are related to the elasticity of the film and have been addressed in the theories of Gibbs and Marangoni. The Gibbs adsorption isotherm relates the lowering of the interfacial tension between two phases, $d\sigma_i$, resulting from the presence of a surface-active solute to the concentration c_i of the solute in the system:

$$-d\sigma_i = \Gamma RT d(\ln c_i) \quad (10.5)$$

where the symbols are as defined previously. The assumption that the concentration of the surfactant can be equated to its activity, while common and useful for simplifying the mathematics, is not always valid at surfactant concentrations far above the critical micelle concentration (**cmc**). Although the Gibbs equation has been employed for the determination of the concentration of surfactants at the oil–water interface, with reasonably good agreement found between experiment and theory, its use is not without difficulties. This is because the attainment of the final equilibrium interfacial concentration of surfactant may be slow and most common experimental methods such as the du Nouy ring, the Wilhelmy plate, and the drop and bubble procedures are dynamic and rely upon an increasing interfacial area during the measurement. Such methods, then, will usually produce results larger than the true equilibrium value.

At equilibrium, the interfacial tension in a system will be uniform. However, in the dynamic environment of an emulsion system, nonuniformities will arise as a result of particle deformations in which new surface area will be produced by deviation of the droplet from a perfectly spherical shape. Since the diffusion of new surfactant molecules to the interface to lower the interfacial tension will require a finite amount of time, interfacial tension gradients will develop, leading to the presence of surface elastic response. If sufficient differences in local interfacial tensions develop, a rapid spreading of surfactant molecules into regions of higher tension will occur. Concurrent with the movement of surfactant into regions of high σ_i , underlying layers of liquid associated with the surfactant may be dragged along.

Surface elasticity in the sense under consideration cannot exist in a system of pure liquid phases. In a system containing surfactant molecules, gradients in interfacial tension can arise as a result of the formation of new area, as mentioned above, or because of the loss of interfacial area. In the former case, the time lag between the formation of new interface and the diffusion of surfactant to that interface will produce an interfacial tension that is higher than equilibrium. The local value of the surface excess Γ_i will fall, and the value of σ_i will approach that of the pure system. The net effect will be a tendency for the interface to contract, providing a “healing” effect to reduce the chance of droplet coalescence. In the case of loss of interfacial area, there will be a time lag from the point of compression of the interfacial film until the excess surfactant molecules can desorb and diffuse away from the interface.

In addition to the Marangoni effect, surface elasticity is affected by what is termed the Gibbs effect, which is concerned with changes in the physical condition of the liquid lamella as two drops approach and begin to touch in the process of flocculation and coalescence. Not only do interfacial tension gradients occur in the film as a result of the finite time required for the adsorption of surfactant molecules at newly formed interface, but also the film will have a limit to which it can be stretched before the lamellar interfacial tension increases to the point where the stabilizing effect of the film is lost. The coefficient of elasticity, E , for an interfacial film under such conditions was given by Gibbs as

$$E = 2A(\delta\sigma_i/\delta A) = 4RT(\sigma_i^2/C)\{1 + \delta \ln \sigma_i / \delta \ln C\} / \{h + 2\delta\sigma_i/dC\} \quad (10.6)$$

where A is the interfacial area occupied by a given quantity of surfactant of concentration C and h is the thickness of the adsorbed film. Calculations using Eq. (10.6) indicate that in a 0.1 M solution of surfactant with a lamellar thickness of 100 nm, the Gibbs coefficient of elasticity will be on the order of 100 mN/m. An extension of the film of 1%, therefore, will result in an increase in the interfacial tension of each side of the film of 1 mN/m. As in the case of the Marangoni effect, the Gibbs elasticity will be significantly affected by the surface activity of the adsorbing species, as indicated by the $(d\sigma_i/d \ln a)$ term.

The experimental determination of the elasticity of lamellar films has, until recently, been difficult, as have studies of the rates of diffusion of surfactant molecules to newly formed interface. It is difficult, therefore, to determine the relative importance of each mechanism in the stabilization of O/W emulsions. New techniques using photon correlation spectroscopy, which can measure the duration and amplitude of surface and interfacial waves, promise to provide a great deal of useful information about the physical properties of such regions as surfaces, interfaces, and lamellar films.

10.5 Mixed Surfactant Systems and Interfacial Complexes

We have seen that the presence of small amounts of surface-active materials can have a dramatic effect on the surface tension of solutions, even those containing relatively larger amounts of other surface-active materials. The classical example of such effects is the minimum in the surface tension/concentration curves found for many anionic sulfate surfactants that contain small amounts of the starting alcohol as an impurity. The action of the impurity may be seen as being twofold; first, because of its less hydrophilic head group (the hydroxyl), the alcohol will be more efficiently adsorbed at the surface; second, because of the smaller size of the head group, the impurity can be packed into the adsorbed layer between adjacent molecules of the primary surfactant, resulting in

a greater surface excess and a lower surface tension. Once the primary surfactant concentration has reached its **cmc**, the less soluble impurity can be solubilized into micelles so that the surface tension will be determined more directly by the primary surfactant species.

In the discussion of foams and foam stability to follow in Chapter 11, it will be seen that the presence of small amount of a surface-active impurity can contribute greatly to foam stability as a result of its effect on lamellar film elasticity. Such a dramatic effect has not been found in the case of emulsion stability against droplet coalescence. Although a limited amount of data is available on the interfacial tension of ternary mixtures, it is generally assumed that surface-active impurities of this type are probably too soluble in the oil phase to remain at the interface. They will be extracted into the oil phase, where they are not particularly surface active and are not strongly adsorbed back into the interface.

In contrast to the insignificant effect of surface-active impurities on emulsion stability, it has been found that the presence of two primary surfactant species, one soluble in water and the other in oil, can greatly enhance the stability of an emulsion system. The effect has been related to the production of very low interfacial tensions and the formation of cooperative surfactant “complexes” that impart greater strength and coalescence resistance to the O/W interface. A broad definition for the term “complex” should be inferred in this context. It is not used, necessarily, to imply some formally identifiable, fixed composition combination of two amphiphiles, but rather a general synergistic effect produced by the combination.

Investigations of the effects of oil-soluble surfactants on the emulsification of paraffins in aqueous surfactant solutions led to the proposal that the formation of interfacial complexes at the oil–water interface could increase the ease with which emulsions could be formed and, possibly, explain the enhanced stability often found in such systems (Figure 10.9). By definition, an interfacial complex is an association of two or more amphiphilic molecules at an interface in a relationship that will not exist in either of the bulk phases. Each bulk phase must contain at least one component of the complex, although the presence of both in any one phase is not ruled out. The complex can be distinguished from such species as mixed micelles by the fact that micelles (and therefore mixed micelles) are not adsorbed at interfaces. According to the Le Chatelier principle, the formation of an interfacial complex will increase the Gibbs interfacial excess Γ_i (Eq. (10.2)) for each individual solute involved, and consequently, the interfacial tension of the system will decrease more rapidly with increasing concentration of either component.

The existence of the interfacial complex is distinct from the situation of simple co-adsorption of oil-soluble and water-soluble surfactants. In the case of co-adsorption, each component will be competing for available space in the interfacial region and will contribute a weighted effect to the overall energy of the system. One could even think of co-adsorption as producing individual and independent “islands” of the two different adsorbed species at the interface with their resulting

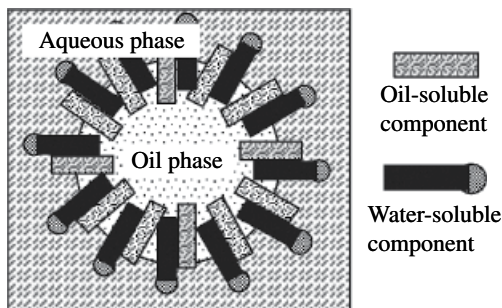


Figure 10.9 A schematic representation of synergistic complex formation at emulsion interfaces.

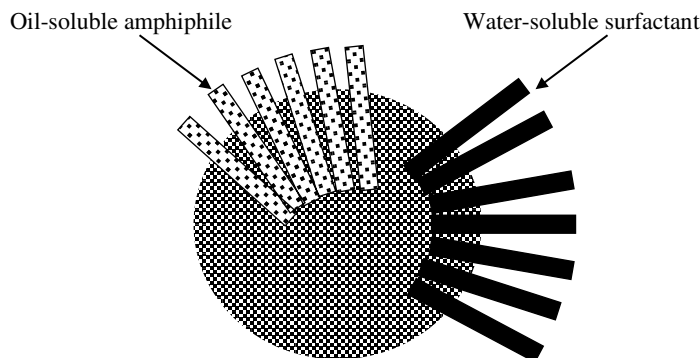


Figure 10.10 “Islands” of co-adsorbed amphiphiles in the interface.

local influences (Figure 10.10). The interfacial complex, on the other hand, implies a more uniform and ordered adsorption pattern for each amphiphilic component resulting in a general interface wide impact, with the net synergistic interfacial effect exceeding that produced by either component or by a simple combination of the two.

Another possible beneficial effect of interfacial complex formation, in addition to the improved surface energetic just mentioned, is that such structures may possess a greater mechanical strength than a simple mixed interfacial layer. Closer molecular packing densities and a greater extent of lateral interaction between hydrophobic chains may result in significant decreases in the mobility of molecules at the interface and a decrease in the rate of drop coalescence. Such an effect has often been mentioned in terms of increased interfacial viscosity or elasticity.

When one discusses the phenomenon of surface elasticity, it is easy to think in terms of the effects of bulk rheological phenomena such as viscosity on the characteristics of a system. In fact, it has been assumed by many that the presence of a high surface viscosity alone can contribute significantly to the stability of an emulsion system. Much of the evidence used to argue in favor of such a role for surface viscosity is related to the rate of film drainage between approaching droplets. In essence it is argued that if a higher interfacial viscosity slows the loss of intervening material between drops, it must therefore enhance the stability of the system to coalescence. In some instances, that stabilizing mechanism may be active, in others not so much so.

In an emulsion system stabilized only by the presence of adsorbed monomeric surfactant species, there have been several arguments put forward against the role of surface viscosity in emulsion stability. In the first place, high interfacial viscosities have very rarely been found in O/W systems not containing a polymeric emulsifier component. Second, because emulsion droplets are very small, tangential shear stresses will produce localized interfacial tension gradients, which will immediately be counteracted by the Marangoni effect. The actual flow of the interfacial film in the thinning process, which could be affected by viscosity, will not occur. If an isolated emulsion droplet is exposed to shear in a flowing field, the front and rear portions of the drop will deform much like the deformation of a water-filled balloon (Figure 10.11), but again, substantial flow in the interfacial region will not occur. If drops are closely spaced, however, the additional interactions induced by the hydrodynamic flow may result in partial destabilization of the interacting drops, leading to flocculation or coalescence. In that case, a given emulsion formulation may, and probably will, have an optimum energy input for formation of the best emulsion beyond which the excess energy results in drop coalescence rather than disruption.

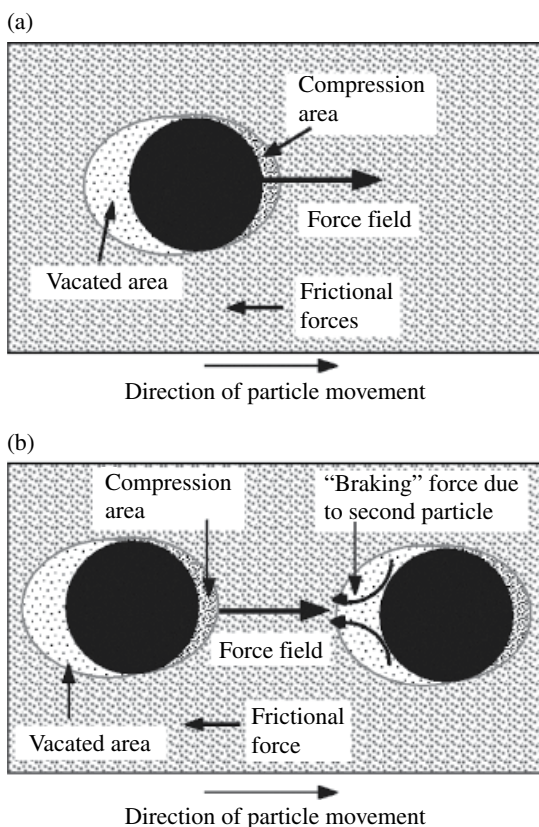


Figure 10.11 The deformation of an emulsion drops in a flowing field: (a) isolated particle and (b) interacting particles.

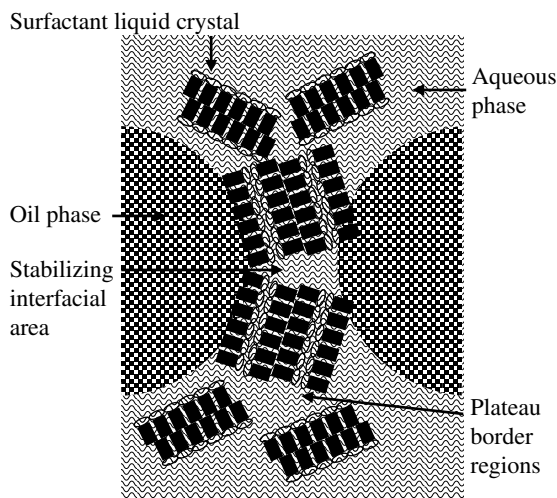
In the presence of polymeric stabilizers, the situation is much more complex and is poorly understood. It can reasonably be assumed, however, that if the stabilizing activity of the adsorbed polymer is based on steric interactions, both the viscosity of the interfacial layer and osmotic forces in the interstitial region between drops will contribute to the overall stabilizing effect.

In conclusion, it appears that the characteristics of the oil–water interfacial film that enhance the kinetic properties or metastability of emulsions in the presence of monomeric surfactant species can be related to their function in the context of the Gibbs–Marangoni effects and the formation of specific interfacial complexes leading to enhanced stability. By damping out local variations in interfacial tension and distortions in the intervening interstitial film, surfactants help maintain a uniform lamellar thinning process between approaching droplets, “healing” local areas of weakness that could lead to droplet coalescence and increasing the stability of the system. Based on current results, the role of interfacial viscosity, in the absence of polymeric species, appears to be minimal.

10.6 Amphiphile Mesophases and Emulsion Stability

The mechanical strength, elasticity, and rheological properties of the interfacial film stabilizing an emulsion obviously have a significant impact on the overall stability of the system. Chapter 7 introduced the concept of liquid crystal and mesophase formation in surfactant systems, usually in the

Figure 10.12 Some potential roles of amphiphilic mesophases at or near emulsion interfaces.



context of increases in the concentration of surface-active material in solution. As indicated, such phases possess a degree of order that produces substantial changes in the properties of the system relative to those of the molecular or simple micellar solutions, including a higher degree of rigidity, larger structural units, and less fluctuation in composition. In view of the mechanisms of emulsion stabilization discussed above, such phases, if present at the O/W interface, might be expected to impart an added degree of stability to systems in which they are present (Figure 10.12). In a practical sense, liquid crystals or other mesophases may be compared with the mixed interfacial complexes discussed in the preceding section, only producing a more complex interfacial situation on a larger scale. The presence of liquid crystals in the region of high drop curvature will also help overcome the Laplace pressure differential.

The presence of liquid crystals or other such structures at or near the oil–water interface has been shown to produce improvements in the stability of numerous emulsions, although the exact mechanism of their action is still subject to some question. Even in the absence of complete understanding (as is often the case for surfactant-related topics), the usefulness of such structures at O/W interfaces has been demonstrated in practical applications.

By analogy with monomolecular films at liquid–air interfaces, surfactants at the liquid–liquid interface will normally form monolayers with various molecular packing densities ranging from relatively loosely packed arrangements normally associated with fluid phases (gases and liquids) to the close-packed solid phase. Classically, amphiphilic adsorption at interfaces has been roughly classified in terms of film types related to normal states of matter (Figure 10.13):

- 1) *Liquid expanded* (L1), in which the adsorbed molecules may assume a variety of orientations with regard to the dividing surface ranging from perpendicular to almost parallel (Figure 10.13a), but with average molecular distances much greater than in bulk liquids and significant rotational disorder in the vertical chains.
- 2) *Liquid condensed* (L2) (Figure 10.13b), in which the adsorbed molecules are relatively close packed with a tilted orientation and reduced chain mobility.
- 3) *Condensed solid* (CS) (Figure 10.13c), in which the adsorbed molecules are close packed with essentially vertical orientation to the interface and minimum mobility – essentially incompressible unless layer collapse occurs.

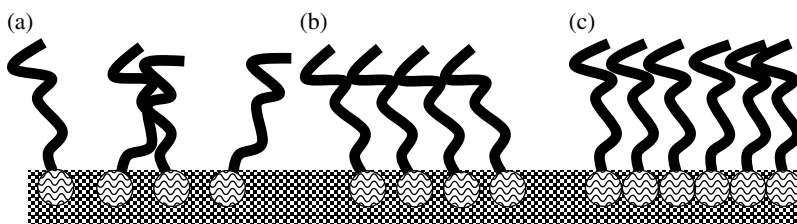


Figure 10.13 Typical forms of monolayer films at L/L and L/V interfaces: (a) moderately close packed with significant chain mobility (liquid expanded), (b) close packed with tilted orientation and reduced chain mobility (liquid condensed), and (c) close packed with essentially vertical orientation and very limited chain mobility (condensed solid).

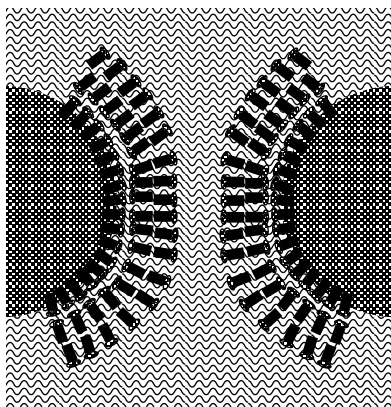


Figure 10.14 The growth of surfactant bilayers at emulsion interfaces.

Although the experimental basis for such a classification stems from monolayer work at the L/V interface, enough correspondence has been found with L/L systems that a high degree of confidence can be placed in the translation of the same concepts to emulsion systems, at least as a first approximation to reality. The presence of liquid phases on each side of the monolayer, the potential for amphiphile movement across the interface, and the complications of solubility in the two phases, all of which will no doubt affect the properties of the monolayer structures, require some flexibility in the interpretation of experimental results.

In L/V monolayers, multilayer formation can be found once the available surface area has been saturated with surfactant molecules or when surface pressures exceed the limit of the system and monolayer collapse occurs. The normal growth process will result in the addition of consecutive layers with alternating surface characteristics. That is, the first monolayer will expose hydrophobic groups, the second hydrophilic, and so on (Figure 10.14). In a L/L situation, growth may be more directly by bilayer units so that the relationship between the two liquid phases and the exposed surfactant groups is maintained. The presence of such multilayer film formation between emulsion droplets will have obvious consequences for the stability of a system.

While there is still some controversy in the literature concerning the exact role of liquid crystals and interfacial complexes in emulsion stabilization. Whether specific association complexes between mixed surfactant or surfactant-additive systems occur at the interface, or whether the results so interpreted are actually produced by some other less specific phenomenon such as enhanced film cohesiveness due to more favorable van der Waals interactions, the net result is that enhanced emulsion stability can be obtained by the proper choice of the materials employed in the formulation.

10.7 Surfactant Structure and Emulsion Stability

Ideally, the world of emulsion formulation would be such that a simple correlation could be obtained between the chemical structure of a surfactant and its performance in practice. Unfortunately, the complicated nature of typical emulsion formulations – the nature of the oil phase, additives in the aqueous phase, specific surfactant interactions, end-use requirements, etc. – makes correlations between surfactant structure and properties in emulsification processes very empirical.

In the absence of a truly quantitative and absolute method for choosing a surfactant for a given application, it is possible to outline a few rules of thumb that have historically proven useful for narrowing down the possibilities and limiting the amount of experimentation that will be required for the final selection of surfactant(s) for a given application. For example, the surfactant(s) must exhibit sufficient surface activity to insure effective and efficient adsorption at the oil–water interface. That activity must also be related to the actual conditions of use – the nature of the oil phase, possible additives in each phase, conditions of temperature and pressure, etc. – and often cannot be inferred directly from activity in water alone. As pointed out previously and again below, the presence of materials such as electrolytes and polymers can greatly alter the functioning of surfactants in stabilizing an emulsion as well as in controlling the type of emulsion formed.

The basic role of the interfacial film between the two phases has already been pointed out. It is clear, then, that the surfactant (or surfactants) employed should produce as strong an interfacial film as possible, one with high viscosity and tenacity, consistent with their ability to produce the required droplet size under the conditions of emulsification. It is useful, therefore, to choose a surfactant system with maximum lateral interaction among the surfactant molecules concurrent with efficient and effective lowering of the interfacial tension.

On a molecular level, the choice of surfactant for a given application must also take into consideration the type of emulsion desired and the nature of the oil phase. As a general rule, water-soluble surfactants yield O/W systems while oil-soluble materials preferentially produce W/O emulsions. Because of the role of the interfacial layer in emulsion stabilization, it is often found that a mixture of surfactants with widely differing solubility properties will produce emulsions with better stability than ones with equivalent concentrations of either material alone. Looking for synergism in mixed surfactant systems can be a very valuable rule of thumb in the absence of more specific guidance. Finally, it is usually safe to say that the more polar the oil phase, the more polar will be the surfactant required to provide optimum emulsification and stability. Such rules of thumb, while having great practical utility, are less than satisfying on a scientific level. One would really like to have a neat, quantitative formula for the design of complete emulsion systems. A number of attempts have been made over the years to develop just such a quantitative approach to surfactant selection, and a brief discussion of some such approaches follows.

10.7.1 The Hydrophile–Lipophile Balance (HLB)

It has been a long-term goal of surfactant chemists and formulators to devise a quantitative way of correlating the chemical structure of surfactant molecules with their surface activity through some quantitative relationship that would facilitate the choice of material for use in a given formulation. Perhaps the greatest success along these lines has been achieved in the field of emulsions; therefore, it is appropriate to discuss the subject in some detail in that context.

The first reasonably successful attempt to quantitatively correlate surfactant structures with their effectiveness as emulsifiers was the hydrophile–lipophile balance (HLB) system. In that

system, the aim is to calculate a number that “measures” the emulsifying potential, in terms of emulsion quality and stability or the so-called HLB, of a surfactant from its chemical structure, and to match that number with the corresponding HLB of the oil phase to be dispersed. The system employs certain empirical formulas to calculate the HLB number, normally giving answers within a range of 0–20 on some arbitrary scale. At the high end of the scale lie hydrophilic surfactants, which possess high water solubility and generally act as good solubilizing agents, detergents, and stabilizers for O/W emulsions; at the low end are surfactants with low water solubility, which act as solubilizers of water in oils and good W/O emulsion stabilizers. The effectiveness of a given surfactant in stabilizing a particular emulsion system would then depend upon the balance between the HLBs of the surfactant and the oil phase involved.

For nonionic surfactants with polyoxyethylene solubilizing groups, the HLB was calculated from the formula

$$\text{HLB} = \text{mol\%hydrophilic group}/5 \quad (10.7)$$

In such a scheme, an unsubstituted polyoxyethylene glycol would have an HLB of 20. HLB values for some typical nonionic surfactants are given in Table 10.1.

Surfactants based on polyhydric alcohol fatty acid esters such as glycerol monostearate can be handled by the relationship

$$\text{HLB} = 20(1 - S/A) \quad (10.8)$$

where S is the saponification number of the ester and A is the acid number of the acid. A typical surfactant of this type, commercially known as Tween 20 [polyoxyethylene (20) sorbitan

Table 10.1 Some calculated HLB values for typical nonionic surfactant structures.

Surfactant	HLB
Sorbitan trioleate	1.8
Sorbitan tristearate	2.1
Propylene glycol monostearate	3.4
Glycerol monostearate	3.8
Sorbitan monooleate	4.3
Sorbitan monostearate	4.7
Polyoxyethylene(2) cetyl ether	5.3
Diethylene glycol monolaurate	6.1
Sorbitan monolaurate	8.6
Polyoxyethylene(10) cetyl ether	12.9
Polyoxyethylene(20) cetyl ether	15.7
Polyoxyethylene(6) tridecyl ether	11.4
Polyoxyethylene(12) tridecyl ether	14.5
Polyoxyethylene(15) tridecyl ether	15.4

Numbers in parenthesis indicate the average number of OE units in the hydrophilic chain.

monolaurate], with $S = 45.5$ and $A = 276$, would have an HLB of 16.7. For materials that cannot be saponified, an empirical formula of the form

$$\text{HLB} = (E + P) / 5 \quad (10.9)$$

can be employed. In the equation, E is the weight percent of oxyethylene chains, and P is the weight percent of polyhydric alcohol (glycerol, sorbitan, etc.) in the molecule.

Although the HLB system has proved to be very useful from a formulation chemist's point of view, its empirical nature did not satisfy the desire of many for a sounder theoretical basis for surfactant characterization. It was subsequently suggested that HLB numbers could be calculated based upon group contributions according to the formula

$$\text{HLB} = 7 + \sum(\text{hydrophilic group numbers}) - \sum(\text{hydrophobic group numbers}) \quad (10.10)$$

Some typical group numbers are given in Table 10.2.

The use of the HLB system for choosing the best emulsifier system for a given application originally required the performance of a number of experiments in which surfactants or surfactant mixtures with a range of HLB numbers are employed to prepare emulsions of the oil in question, and the stability of the resulting emulsions is evaluated by measuring the amount of creaming that occurred with time. The use of surfactant mixtures can become complicated by the fact that such mixtures often produce more stable emulsions than a single surfactant with the same nominal HLB number. The HLB of a mixture is assumed to be an algebraic mean of the HLBs of the components

$$\text{HLB}_{\text{mix}} = f_A \times \text{HLB}_A + (1 - f_A) \times \text{HLB}_B \quad (10.11)$$

where f_A is the weight fraction of surfactant A in the mixture. It has been found experimentally, however, that such a linear relationship for nonionic mixtures is observed only when each component of the mixture is able to act independently of the other, with no specific molecular interactions occurring. A number of studies have indicated significant deviations from linearity, both positive and negative, based on emulsion stability tests, interfacial tension measurements, and

Table 10.2 Typical group numbers for the calculation of HLB numbers.

Group	HLB number	Group	HLB number
Hydrophilic		Hydrophobic	
—SO ₄ Na	38.7	—CH—	−0.475
—COOK	21.1	—CH ₂ —	−0.475
—COONa	19.1	—CH ₃	−0.475
—N (tertiary amine)	9.4	=CH—	−0.475
Ester (sorbitan)	6.8	—CF ₂ —	−0.87
Ester (free)	2.4	—CF ₃	−0.87
—COOH	2.1	Miscellaneous	
—OH (free)	1.9	—(CH ₂ CH ₂ O)—	0.33
—O—	1.3	—(CH ₂ CH ₂ CH ₂ O)—	−0.15
—OH (sorbitan)	0.5		

correlations using gas–liquid chromatography, cloud point determinations, and phase inversion temperature (PIT) data (see below).

Although going a long way toward simplifying the choice of surfactants for the stabilization of a given oil in water, the HLB system does not always provide a clear-cut answer for a given system. It does not, for example, take into consideration the effects of a surfactant on the physical properties of the continuous phase, especially its rheological characteristics. As noted previously, the viscosity of the continuous phase will significantly affect the rate of creaming, as will alterations in the relative densities of the two phases. As a result, it is possible to prepare very stable emulsions with surfactants whose HLB numbers lie well away from the “optimum” that would be predicted by the performance of a series of HLB-related experiments. Its obvious faults notwithstanding, the HLB system as originally derived and subsequently expanded has found extensive practical use. Especially when applied to nonionic surfactants and their mixtures, the concept appears to possess some fundamental rationality that has yet to be revealed completely at the molecular level.

One approach to the establishment of a sounder theoretical basis for the HLB number concept (in aqueous systems, at least) has been the relationship between HLB and the degree of hydration of the surfactant molecule, as expressed by the Hildebrand solubility parameter or cohesive energy density (δ_H). The concept is that the solubility and surface activity of a given surfactant structure can be quantitatively related to the “critical” HLB number for the emulsification of a given oil phase in aqueous solution by its solubility parameter or cohesive energy density in water. The efficiency of a surfactant at emulsifying and stabilizing an oil phase will be a function of the relative degrees of interaction of the various portions of the surfactant molecule with the oil and aqueous phases. The original concepts of HLB were, as seen above, based on a simple ratio of hydrophilic to hydrophobic groups in the molecule. With the introduction of Hildebrand solubility parameters as a more quantitative way to calculate the solubility of materials, especially polymers, in various solvents, an attempt was made to relate the HLBs of a number of surfactants to their calculated δ_H . Their results fitted the relationship

$$\delta_H = \{243/(54 - \text{HLB})\} + 12.3 \quad (10.12)$$

where δ_H , in SI units, is in (MPa^{1/2}).

More complicated treatments used three-dimensional Hansen parameters to relate the emulsifying tendencies of surfactants with oils in terms of the ratios of the cohesive energies of the oil and the hydrophobic portion of the surfactant molecule and that of the water with the hydrophilic portion. In that concept, the best result can be expected when the various components of the cohesive energy density of the three phases – oil, water, and surfactant – are matched. The dispersion (d), polar (p), and hydrogen bonding (h) portions of the three-dimensional solubility parameters are, to a first approximation, related by

$$\delta_H^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad (10.13)$$

so that division of Eq. (10.13) by δ_H^2 will lead to

$$1 = f_d + f_p + f_h \quad (10.14)$$

where f is that fraction of the total solubility parameter attributable to each type of interaction. Using that relationship, it is possible to construct a triangular diagram that can relate the δ 's of each component and serve as a useful predictive tool for emulsion formulation. Unfortunately, the

utility of such an approach is somewhat limited by the scarcity of experimental data for most surfactant structures and the complications introduced by the complex and sometimes varied compositions of many industrial surfactants.

When all of the component solubility parameters of the oil and the surfactant are matched, a relationship between HLB and chemical composition of the form

$$\text{HLB} = 20M_h / (M_l + M_h) \quad (10.15)$$

results, where M_h is the molecular weight of the hydrophilic portion of the molecule (including the carbon atom of a carboxyl group) and M_l is that of the hydrophobe or lipophile.

Because the “effective” HLB of a given surfactant will depend on the nature of the solvent, HLB numbers cannot be considered to be absolute, realistic measures of the emulsifying ability of a material under all conditions. The actual HLB of a surfactant in a system will depend on the nature of the solvent, the temperature, and the presence of additives such as cosolvents, electrolytes, and polymers. Although the relationship will not always be linear, the HLB may be expected to vary in a manner analogous to that found for the **cmc** of the surfactant under the same conditions.

Using the HLB group calculation approach, the HLB and **cmc** of a surfactant can be related through a relationship of the form

$$\ln(\text{cmc}) = C_1 + C_2(\text{HLB}) \quad (10.16)$$

where the constants C_1 and C_2 are characteristics related to a homologous series of surfactants. Using that formulation, it is possible to define a relationship between the free energy of micellization for a surfactant and its HLB in water. Combining the relevant equations yields

$$\text{HLB} = C_1 + C_2(\Delta G_m/RT) \quad (10.17)$$

Further separation of ΔG_m into its hydrophilic and hydrophobic components allows one to write

$$\text{HLB} = C_1 + C_2(\Delta G_{mh}/RT) + C_2(\Delta G_{ml}/RT) \quad (10.18)$$

It can be seen that Eq. (10.18) is formally equivalent to equation (Eq. (6.21)). In this way, the concept of the HLB can be associated with the tendency of a surfactant to aggregate or adsorb at interfaces. It has been found that a reasonably linear relationship between HLB and ΔG_m can be obtained, with slopes varying according to the nature of the hydrophilic and hydrophobic groups, as would be expected from the relationships discussed in Chapter 6.

As already pointed out in Chapters 6 and 7, geometrical constraints imposed by the particular molecular characteristics of a surfactant molecule control the formation of aggregates (size, shape, curvature, etc.). The previously defined geometric packing parameter $P_c = v/a_o l_c$, where v is the volume of the hydrophobic group, a_o is the optimum head group area, and l_c is the critical length of the hydrophobe, can be viewed as a type of HLB number, being based on volume fraction instead of weight fractions of hydrophobe and the geometry of the hydrophobic chain. In that case, P_c could be considered an “inverse” HLB (HLB_i), where

$$\text{HLB}_i = 20 - \text{HLB} \quad (10.19)$$

By use of geometric considerations, it can be seen that the value of P_c determined from molecular geometry should predict the type of emulsion formed by a particular surfactant. For instance, for

$P_c < 1$, the curvature of the oil–water interface should be concave toward the oil phase, leading to an O/W emulsion. For $P_c > 1$, the reverse would be expected. At $P_c = 1$, a critical condition would be expected where phase inversion would occur or multiple emulsion formation would be favored (see below).

From the above discussion, it should be clear that, theoretical “desires” notwithstanding, the goal of a quantitative magic formula for calculating the surfactant characteristics needed for a given emulsion remains elusive. As has been seen for other surfactant applications, simple answers only apply in simple systems, and simple systems are not, unfortunately, the rule in practice. While HLB numbers, solubility parameters, and geometric factors provide extremely useful approaches for making an educated guess about a surfactant or surfactants to use in a formulation, the final answer will still require old fashioned, hands-on experiments to find the best of all worlds. And that best answer will no doubt be significantly influenced by the presence of other actors on the stage.

10.7.2 Phase Inversion Temperature (PIT)

Several references were made above to the term “phase inversion temperature.” With the exceptions of Eqs. (10.17) and (10.18), however, no specific reference was made to the effect of temperature on the HLB of a surfactant. From the discussions in Chapter 6, it is clear that temperature can play a role in determining the surface activity of a surfactant, especially nonionic amphiphiles in which hydration is the principal mechanism of solubilization. The importance of temperature effects on surfactant solution properties, especially the solubility or cloud point of nonionic surfactants, led to the evolution of the concept of using that property as a tool for predicting the activity of such materials in emulsions. Since the cloud point is defined as the temperature, or temperature range, at which a given amphiphile loses sufficient solubility in water to produce a “normal” surfactant solution, it was assumed that such a temperature-driven transition would also be reflected in the role of the surfactant in emulsion formation and stabilization.

In this case, it was felt that the phenomenon would result in an “inversion” of the role of the material in terms of the type of emulsion favored by its presence. For example, at low temperatures, a given material would be expected to be an O/W emulsifier, while at temperatures above the cloud point, it would become a W/O emulsifier. In the context of emulsion technology, therefore, the cloud point phenomenon became known as the phase inversion temperature of the surfactant and was proposed as a quantitative approach to the evaluation of surfactants in emulsion systems. In effect, the PIT is not a characteristic of a surfactant, but rather a characteristic of the complete emulsion system.

The general procedure developed for the evaluation system was as follows: emulsions of oil, aqueous phase, and approximately 5% surfactant were prepared by shaking at various temperatures. The temperature at which the emulsion was found to be inverted from O/W to W/O was then defined as the PIT of the system. Since the effect of temperature on the solubility of nonionic surfactants is reasonably well understood, the physical principles underlying the PIT phenomenon followed directly.

It is generally found that the same circumstances that affect the solution characteristics of nonionic surfactants (**cmc**, micelle size, cloud point, etc.) will also affect the PIT of emulsions prepared with the same materials. For typical POE surfactants, increasing the length of the POE chain will result in a higher PIT, as will a broadening of the POE chain length distribution. The use of PIT, therefore, represents a potentially useful tool for the comparative evaluation of emulsion stability. Many reports of its use in the emulsion technology field are available.

Because the PIT approach to surfactant evaluation is newer than the HLB method, the effects of variables on the relationship between PITs, surfactant structures, and emulsion stability have not been as clearly defined in a quantitative way. It has been found, however, that there is an almost linear correlation between the HLB of a surfactant under a given set of conditions and its PIT under the same circumstances. In essence, the higher the HLB of the surfactant system, the higher will be its PIT.

The sensitivity of emulsions to temperature led to the suggestion that the PIT phenomenon could also be used as a convenient method for emulsion preparation. In such a procedure, an emulsion is prepared very near the PIT of the system (routinely $\pm 4^\circ$), where minimum droplet sizes can normally be obtained. The emulsion is then cooled to its storage or use temperature, where enhanced stability usually results. In nonionic systems particularly, such an approach to emulsion preparation can provide advantages in terms of the energy required for emulsification in addition to providing enhanced stability.

Because the PIT appears to be directly related to the HLB of the surfactant, the effects of such factors as surfactant concentration, oil phase polarity, additives, and phase ratios would be expected to parallel what has been observed for HLB determinations. Certainly, it can be expected that much more information will be published in the coming years, which will allow for a better understanding of the relationships between these two concepts of surfactant evaluation.

10.7.3 Application of HLB and PIT in Emulsion Formulation

The choice of a particular emulsifier system for an application will depend on several factors, some of which will be chemically related (optimum HLB, PIT, etc.), while others will be driven by three “e’s” of business: economic, environmental, and esthetic factors. The relative value of the latter will depend mostly on price and value-added considerations for each individual system. Here we are concerned only with the chemical aspects of emulsion formation and stabilization. In most general applications, the HLB system has been found most useful in guiding the formulator to a choice of surfactant most suited to individual needs. Table 10.3 lists the ranges of HLB numbers that have proved to be most useful for various applications.

Obviously, the ranges in which surfactants of various HLBs can be employed are quite broad. Specific requirements for many systems have been tabulated in the works cited in the chapter bibliography. While such tabulations can be very useful to the formulations chemist, it must be kept in mind that there is nothing particularly magic about a given HLB number. Many surfactants or surfactant mixtures may possess the same HLB, yet subtle differences in their chemical structures, solution chemistry, and specific interactions with other system components may result in significant differences in performance. Particularly important may be the formation of interfacial

Table 10.3 HLB ranges and their general areas of application.

HLB range	General applications
2–6	W/O emulsions
7–9	Wetting and spreading
8–18	O/W emulsions
3–15	Detergency
15–18	Solubilization

Table 10.4 HLB numbers for typically encountered oil phases.

Oil phase	Nominal HLB
Lauric acid	16
Oleic acid	17
Cetyl alcohol	15
Decyl alcohol	14
Benzene	15
Castor oil	14
Kerosene	14
Soybean oil	13
Lanolin	12
Carnauba wax	12
Paraffin wax	10
Beeswax	9

complexes, as noted above. Even though the additive nature of surfactant mixture HLBs (Eq. (10.11)) has not been found to be linear over a wide range of compositions, over the short range of one or two HLB units usually encountered in formulation work, linearity can usually be assumed with little risk. It is therefore possible, in most cases, to fine-tune a surfactant mixture with a minimum of experimental effort.

As alluded to above, one approach to the application of surfactant HLB to formulation is to match that of the surfactant to the oil phase being employed. The HLB of the oil can be determined empirically or calculated using the procedures discussed previously. It is usually found that the additivity principle will hold for mixtures of oils in a way similar to that for surfactants, possibly even to the extent of nonlinearity in cases where oil structures differ significantly. Therefore, in formulating an emulsion, it is possible to determine the HLB of the oil phase and to vary the surfactant or mixture HLB to achieve the optimum performance. HLB numbers of some commonly used oil phases are given in Table 10.4.

It should be noted that HLB numbers are most often used in connection with nonionic surfactants. While ionic surfactants are included in the HLB system, the more complex nature of the solution properties of the ionic materials makes them less amenable for the normal approaches to HLB classification. In cases where an electrical charge is desirable for stability or for some other functional reason, it has been suggested that surfactants having limited water solubility and a bulky hydrophobic structure that inhibits efficient packing into micelles should be most effective as emulsifiers. Surfactants such as the sodium trialkyl naphthalene sulfonates and dialkylsulfosuccinates, which do not readily form large micelles in aqueous solution, have found use in that context, usually providing advantages in droplet size and stability over simpler materials such as sodium dodecyl sulfate.

Clearly, the process of selecting the best surfactant or surfactants for the preparation of an emulsion has been greatly simplified by the development of the more or less empirical, semiquantitative approaches exemplified by the HLB and PIT methods described above. Unfortunately, each method has its limitations and cannot eliminate the need for some amount of trial-and-error

experimentation. As our fundamental understanding of the complex phenomena occurring at oil–water interfaces improves, and the effects of additives and environmental factors on those phenomena become clearer, it may become possible for a single, comprehensive theory of emulsion formation and stabilization to lead to a single, quantitative scheme for the selection of the proper surfactant system.

10.7.4 The Effects of Additives on the “Effective” HLB of Surfactants

The exact mechanisms by which various additives affect the effective HLBs of surfactants are not fully understood. For nonionic POE surfactants, in which hydration of the POE chain is the primary solubilizing mechanism in aqueous solution, the extent of chain hydration has not generally been found to be increased by the addition of materials that “salt in” the surfactants. That conclusion is based on the observation that the viscosity of the solutions is not significantly affected, indicating that the hydrodynamic radius of the molecules is not increased by increased hydration. In fact, the actions of such additives are in all probability related to their effects on the structure of the solvent, altering the thermodynamics of the solvent–solute interactions.

A proposed relationship between the HLB and the heat of hydration, Q_h , of a surfactant is given by

$$\text{HLB} = 0.42Q_h + 7.5 \quad (10.20)$$

where Q_h is given in calories per gram. From Eq. (10.20), it seems that the addition of materials that increase the heat of hydration, such as sodium thiocyanate, should produce an increase in the effective HLB of the surfactant. Such an effect is found for nonionic surfactants in aqueous thiocyanate solution compared with those in the presence of “salting-out” additives such as sodium chloride.

In the case of nonionic surfactants, the steric or enthalpic barrier to droplet coalescence produced by the hydrated hydrophilic chain is a major factor in emulsion stability. The addition of additives that increase the heat of hydration should result in an increase in the enthalpic contribution to stability. Experimentally, unambiguous evidence to support such a hypothesis has been difficult to obtain.

The difficulty of obtaining good experimental evidence for the correlation of increased cloud points for nonionic surfactants and their effectiveness as emulsion stabilizers may be related to the fact that surfactant interactions at interfaces, as well as their own self-aggregation characteristics, are affected in very complex ways by the presence of additives. As discussed in Chapter 6, the solubility and **cmc** of a given surfactant depend strongly on the nature of the solvent and additives, as does the adsorption of molecules at various interfaces. If there is an optimum HLB for a given oil that produces maximum stability, any additive that alters the solution properties of the surfactant should also alter the effective HLB of the surfactant and, therefore, shift it away from the optimum value.

Some studies have tried to follow the factors controlling the effective HLB of specific systems, varying the surfactant, the oil, and the continuous phase in a regular way. By monitoring such factors as emulsion droplet size, emulsion rheology, creaming, and inversion temperatures, they determined that additives that acted as “salting-in” agents produced a decrease in the critical HLB needed for maximum stability. “Salting-out” additives had the opposite effect.

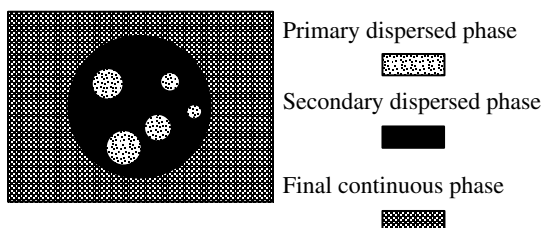


Figure 10.15 A schematic representation of a multiple emulsion.

10.8 Multiple Emulsions

While a great deal of information has been published over the years on the theoretical and practical aspects of emulsion formation and stabilization, until recently little has been said about more complex systems generally referred to as multiple emulsions. Multiple emulsions, as the name implies, are composed of droplets of one liquid dispersed in larger droplets of a second liquid, which are then dispersed in a final continuous phase (Figure 10.15). Typically, the internal droplet phase will be miscible with or identical to the final continuous phase. Such systems may consist of a W/O/W dispersion, where the internal and external phases are aqueous, or O/W/O multiple emulsions that have the reverse structure. Although known for almost a century, such systems have only recently become of practical interest for possible use in controlled drug delivery, emergency drug overdose treatment, wastewater treatment, and separations technology. Other useful applications will no doubt become evident as our understanding of the physical chemistry of such systems improves.

Because they involve a variety of phases and interfaces, multiple emulsions will be inherently more unstable than simple emulsions. Their surfactant requirements are such that two stabilizing systems must be employed – one for each oil–water interface. Each surfactant or mixture must be optimized for the type of emulsion being prepared but must not interfere with the companion system designed for the opposite interface. Long-term stability, therefore, requires careful consideration of the characteristics of the various phases and surfactant solubilities.

10.8.1 Nomenclature for Multiple Emulsions

For systems as potentially complex as multiple emulsions, it is very important that a clear and consistent system of nomenclature be employed. For a W/O/W system, for example, in which the final continuous phase is aqueous, the primary emulsion will be a W/O emulsion, which is then emulsified into the final aqueous phase. The surfactant or emulsifier system used to prepare the primary emulsion is referred to as the primary surfactant, and the volume fraction of the primary dispersed phase is the internal aqueous phase of the final multiple emulsion. Subscripts are used to further avoid ambiguities as to components or their locations in the system. For example, in a W/O/W system, the aqueous phase of the primary emulsion would be denoted as W_1 and the primary emulsion as W_1/O . After the primary emulsion has been further dispersed in the second aqueous phase W_2 , the complete system is denoted $W_1/O/W_2$. In the case of an O/W/O multiple emulsion, the notation is $O_1/W/O_2$. Additional refinements to fit even more complex systems, including the “order” of multiple emulsions, have been suggested.

10.8.2 Preparation and Stability of Multiple Emulsions

In principle, multiple emulsions can be prepared by any of the many methods for the preparation of conventional emulsion systems, including sonication, agitation, and phase inversion. Great care

must be exercised in the preparation of the final system, however, because vigorous treatments normally employed for the preparation of primary emulsions will often break the primary emulsion, resulting in loss of phase identity.

Multiple emulsions have reportedly been prepared conveniently by the phase inversion technique mentioned earlier; however, such systems have generally been found to have limited stability. It generally requires a very judicious choice of surfactant or surfactant combinations to produce a multiple emulsion system that has useful characteristics of formation and stability. A general procedure for the preparation of a W/O/W multiple emulsion may involve the formation of a primary emulsion of water in oil using a surfactant suitable for the stabilization of such W/O systems. Generally, that will involve the use of an oil-soluble surfactant with a low HLB (2–8). The primary emulsion will then be emulsified in a second aqueous solution containing a second surfactant system appropriate for the stabilization of the secondary O/W emulsion (HLB 6–16). As noted above, because of the possible instability of the primary emulsion, great care must be taken in the choice of the secondary dispersion method. Excessive mechanical agitation such as in high-speed mixers and sonication could result in gross coalescence of the primary emulsion and the production of essentially “empty” oil droplets. The evaluation of the yield of filled secondary emulsion drops, therefore, is very important in assessing the value of different preparation methods and surfactant combinations.

The nature of the droplets in a multiple emulsion will depend on the size and stability of the primary emulsion. A system of classification has been proposed dividing W/O/W multiple emulsions into three classes based upon the nature of the oil phase droplets (Figure 10.16). Type A systems are characterized as having one large internal drop essentially encapsulated by the oil phase. Type B systems contain several small, well-separated internal drops, and systems of type C contain many small internal drops in close proximity. It is understood that any given system will in all probability contain all three classes of drops, but one will be found to dominate, depending primarily on the surfactant system employed.

10.8.3 Pathways for Primary Emulsion Breakdown

There are several possible pathways for the breakdown of multiple emulsions. A few are shown schematically in Figure 10.17. Although all possible mechanisms for droplet coalescence cannot

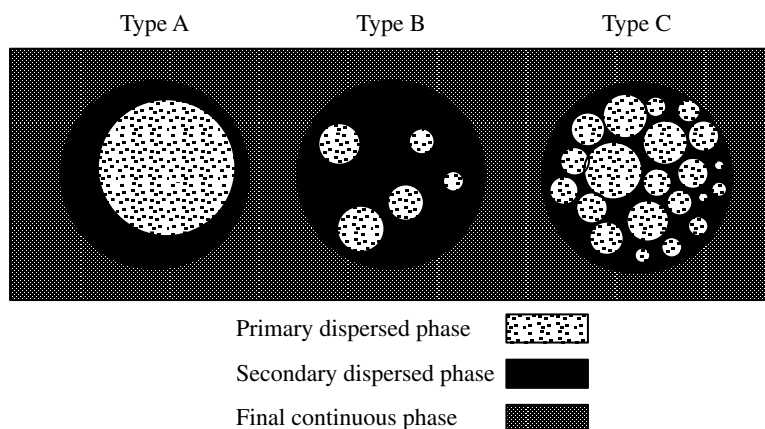


Figure 10.16 Multiple emulsion classification based on droplet characteristics in the primary emulsion.

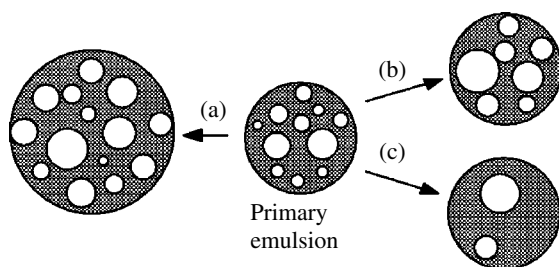


Figure 10.17 Some possible pathways for the breakdown of multiple emulsions: (a) coalescence of secondary emulsion drops, (b) coalescence of primary emulsion drops, and (c) loss of primary emulsion dispersed phase to external phase.

be conveniently illustrated in a single figure, a consideration of just a few possibilities can help clarify the reasons for instability in a given system. Even though there may be a number of factors involved, one of the primary driving forces will be, as always, a reduction in the free energy of the system through a decrease in the total interfacial area. As has been noted previously, a major role of surfactants at any interface is to reduce the interfacial energy through adsorption. In a typical multiple emulsion system, the primary mechanism for short-term instability will usually be drop-let coalescence in the primary emulsion. It will be important, then, to select as the primary emulsifier a surfactant or combination of surfactants that provides maximum stability for that system, whether W/O or O/W.

A second important pathway for the loss of “filled” emulsion droplets is the loss of internal drops by the rupture of the oil layer separating the small drops from the continuous phase. Such an expulsion mechanism would be expected to account for the loss of larger internal droplets. Unless the two phases are totally immiscible (in fact, a rare situation), there will always exist the possibility that osmotic pressure differences between the internal and continuous portions of the system will cause material transfer to the bulk phase. The high pressures in the smaller droplets would be expected to provide a driving force for the loss of material from smaller drops in favor of larger neighbors (Ostwald ripening), as well as to the continuous phase. Finally, the presence of an oil-soluble surfactant always raises the possibility of nonaqueous reversed micelle formation and the subsequent solubilization of internal aqueous phase in the oil. Such a solubilization process also represents a convenient mechanism for the transport of material between the two similar phases.

In the context of a critical application such as controlled drug delivery, in which the mechanism of delivery is diffusion controlled, such breakdown mechanisms would be very detrimental to the action of the system, since they could result in a rapid release of active solute with possibly dangerous effects.

The proposed mechanisms of emulsion breakdown, as well as others, must be addressed in order to understand and control a particular multiple emulsion system. In all cases, the final stability of the system will depend on the nature of the oil phase of interest, the characteristics of the primary and secondary emulsifier systems, and the relationship between the internal and continuous phases.

10.8.4 The Surfactants and Phase Components

Choice of surfactants for the preparation of multiple emulsions can, in principle, be made from any of the four classes of surfactants discussed in Chapter 2. The choice will be determined by the characteristics of the final emulsion type desired: the natures of the various phases, additives,

solubilities, etc. In many applications (e.g. foods, drugs, cosmetics), the choice may be further influenced by such questions as toxicity, interaction with other addenda, and biological degradation. For that reason, well-studied nonionic surfactants have received a great deal of attention for such applications. In a given system, different types of surfactant may produce different types of multiple emulsions (A, B, or C types) so that such questions must also be considered.

As stated earlier, two surfactants or combinations of surfactants must be employed for the formation of multiple emulsions: one for the preparation of the primary emulsion (an oil-soluble system for a final W/O/W emulsion, for example), and a second of a significantly different nature for the final emulsification step. Most attempts to design a system for surfactant choice employ the HLB system to determine the optimum surfactants for both the primary and secondary emulsions. For the production of a W/O/W emulsions, they employ a series of surfactants with HLB numbers in the range of 2–8, typical for the formation of W/O emulsions, as the primary emulsifier, and those in the range of 6–16 for the secondary stage. The evaluation of emulsion stability based upon creaming leads to the optimum choice of surfactant for each stage of the preparation. It has been noted, however, that although useful, the HLB concept as a basis for surfactant choice is limited by the fact that other factors such as viscosity and concentration effects cannot be easily evaluated.

The nature of the oil phase and its specific interactions with the surfactant can significantly affect the emulsion characteristics of the system. The polarity of the oil phase (e.g. fatty esters vs. hydrocarbon oils) will determine the proper surfactant solubility requirements and HLB for the primary emulsion, the mutual solubility of the various components, and the transport of materials from the internal to the external phases. The choice of the optimum HLB for the secondary emulsifier can be strongly affected by the concentration of the primary emulsifier employed. For a single-component secondary emulsifier in a $W_1/O/W_2$ multiple emulsion, the HLB required to provide maximum multiple emulsion stability is found to increase as the concentration of primary emulsifier in the system increases. Since the HLB of the oil phase of the primary emulsion is not changed, the results are explained in terms of the migration of excess or “free” primary emulsifier to the secondary O/W_2 interface. The result is the production of an “effective” HLB at the secondary emulsion interface, which can be related to the final mixed emulsifier composition by Eq. (10.11).

The composition of the primary emulsion dispersed phase may have a significant effect on the overall stability of a system, especially when interactions between the components and surfactant are possible, or when the components themselves may be somewhat surface active. In most instances of multiple emulsion formulation, the internal primary and external secondary phases will be similar in that each will be aqueous or an oil, but the nature of addenda included in each will differ. In particular, there may be significant differences in the level and nature of organic additives and electrolytes present that could alter the stability of the total system.

Electrolytes in particular can exhibit significant effects on the stability of emulsions prepared with one or more ionic surfactants. There are multiple potential effects, including (i) changes in the role of the surfactant at the various interfaces as a result of changes in their electrical properties, (ii) changes in the nature of the interfacial films due to the presence of specific ionic interactions between surfactant and electrolyte, and (iii) alterations in the transport properties of the intervening phase due to differences in the osmotic pressure between the two phases.

The role of electrolytes in affecting the interfacial characteristics of surfactants has already been mentioned in several contexts. In the second instance, the presence of excess ionic species in the internal phase of a $W_1/O/W_2$ emulsion could lead to a closer packing of surfactant molecules at the interface and the erection of a more rigid barrier to the transport of molecules into the oil phase, a potentially useful device for the control of additive release from W_1 .

A major imbalance in the osmotic pressure between internal and external aqueous phases as a result of a high electrolyte content internally would result in a driving force for the movement of water into the primary emulsion. The net result would then be a swelling of the internal droplets and, ultimately, rupture to release the components to the continuous phase. When such catastrophic release of the internal components is unacceptable, the introduction of a neutral electrolyte into the outer phase can reduce the osmotic pressure differences and retard the overall process. Other additives such as synthetic polymers and proteins can perform a similar role in either W/O/W or O/W/O emulsions.

An additional aspect of the nature of the surfactant and its role in stabilizing a multiple emulsion is the formation of liquid crystal phases at the interfaces. It has been found, for example, that the presence of liquid crystal phases greatly enhances the stability of certain O/W/O and W/O/W emulsions. Such systems will generally impart improved stability to coalescence as well as a barrier to the transport of material from one phase to another. Typically, an emulsion may be prepared at a temperature where the surfactant has favorable emulsifying properties followed by cooling to a temperature where liquid crystal formation occurs.

Clearly, multiple emulsions represent a fertile field of research in both applied and academic surface science. Although there are an ever-increasing number of publications appearing on the subject, the area remains somewhat empirical in that each system is highly specific. As yet there are few general rules to guide the interested formulator in the selection of the optimum surfactants for a given application. Cubic bicontinuous phases discussed in Chapter 7 appear to offer some of the same potential advantages sought in multiple emulsion systems. A great deal remains to be done in understanding the colloidal stability of such complex systems and the effects of the various components in each phase on overall multiple emulsion preparation and stability. A sound understanding of the role of surfactants in simple emulsions and an intuitive feel for the effect of the multiple interfaces present on system operation seem to provide the best guidance at the present time.

11

Foams and Liquid Aerosols

It was pointed out earlier that foams and emulsions are related in that they represent a physical state in which one fluid phase is finely dispersed, relatively speaking, in a second phase, the state of dispersion and the long-term stability (persistence) normally being dependent on the presence of one or more additives that alter the energy of the interface between the two phases. In emulsions, each phase is a liquid, so such factors as the solubility of additives in each phase must be considered. In foams, one phase (the dispersed phase) is a gas, so problems related to transfer of materials from the continuous to the dispersed phase effectively do not exist.

Liquid aerosols are, of course, the inverse of foams – liquid drops dispersed in a gas. However, the “nature of the beast” in the case of aerosols pretty much precludes any significant surfactant effects beyond that of affecting the particle size produced at the atomization stage. Some aspects of liquid aerosol technology are presented below. For the most part, however, this chapter addresses the basic role of surfactants in the formation and stabilization of foams and gives some leads as to surfactant properties that may be useful for the suppression or elimination of foams where their presence would be considered detrimental.

The presence of foam in a product or process may or may not be desirable. Foams have wide technical importance in such fields as fire fighting, polymeric foams, and foam rubbers; in foamed structural materials such as concrete; and, of course, in a myriad of food products. They also have certain esthetic utility in many detergent and personal care products, although their presence may not add much to the overall effectiveness of the process. Foams also serve useful purposes in industrial processes such as mineral separation (froth flotation) and for environmental reasons for the suppression of liquid and vapor emissions in some processes such as electroplating. In the latter case, the presence of a foam blanket over the electroplating solution helps prevent solution splattering and the loss of volatile materials, therefore reducing the costs of maintaining an acceptable working environment.

Unwanted foams may be a significant problem in many technical processes, including sewage treatment, coating applications, and crude oil processing. By understanding the physical and chemical characteristics of materials that produce and sustain foams, it becomes easier to identify ways to counteract or overcome those foaming tendencies. The following sections cover some of the basic physical principles of foam formation and stabilization and discuss the molecular requirements of surfactants employed in foam formation or foam suppression.

As is so often the case in discussions of surfactants and their applications, the overwhelming bulk of the information available is based on results in water or aqueous solvent systems.

The following material, therefore, concentrates on such systems. Foaming in nonaqueous systems is less commonly encountered, although the same physical principles would apply in such cases.

11.1 The Physical Basis for Foam Formation

The basic anatomy of a foam is illustrated schematically in Figure 11.1. Because they are encountered in so many important technological areas, foams have been the subject of a significant amount of discussion in the literature. A number of reviews published over the years that cover most aspects of foam formation and stabilization are listed in the Bibliography. While the theoretical aspects of foam stabilization are reasonably well worked out, a great deal remains to be understood concerning the details of surfactant structural relationships to foam formation, persistence, and prevention. The physical nature of foams is quite complicated, and conflicting explanations for foam stability found throughout the literature can sometimes be attributed to unwarranted extrapolations of data, overgeneralization, experimental anomalies, and, of course, honest differences in interpretation. It has been pointed out several times that the bane of the surfactant chemist is quite often the presence in a system of unwanted or unidentified amphiphilic materials. The presence of small amounts of unreacted starting materials, reaction by-products, chemical homologues, etc. can thwart even the most careful experimentalist, and the possibility of the existence of such circumstances must always be considered.

Foams, like almost all systems containing two or more immiscible phases, involve thermodynamic conditions in which the primary driving force is to reduce the total interfacial area between

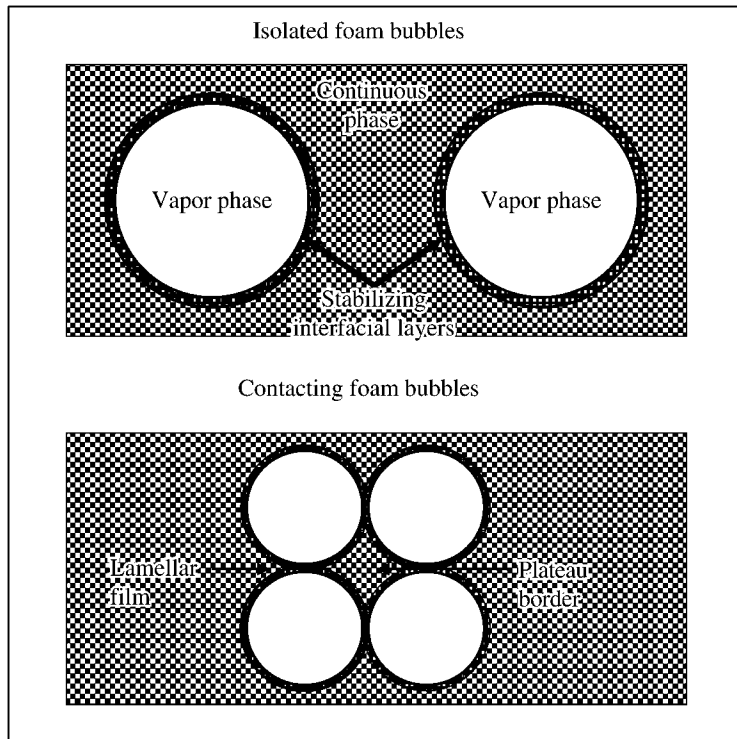


Figure 11.1 The basic anatomy of a foam structure.

the phases – that is, the systems are thermodynamically unstable. The amount of thermodynamically reversible work required to create an interface is given by

$$W = \sigma_i \Delta A \quad (11.1)$$

where W is work in mJ, σ_i is surface tension in mJ/m², and A is in m².

In spite of their tendency to collapse, however, foams can be prepared that have a lifetime or “persistence” of minutes, days, or even months. The reasons for such extended lifetimes can be one or several of the following: (i) a high viscosity in the liquid phase, which retards drainage of the liquid from between the bubble interfaces, as well as providing a cushion effect to absorb shocks resulting from random or induced motion; (ii) a high surface viscosity, which also retards liquid loss from between interfaces and dampens film deformation prior to bubble collapse; (iii) surface effects such as the Gibbs and Marangoni effects (see Chapters 5 and 10), which act to “heal” areas of film thinning due to liquid loss; and (iv) electrostatic and steric repulsion between adjacent interfaces due to the adsorption of ionic and nonionic surfactants, polymers, etc.

In general, one can define three classes of foams: unstable, “metastable,” and solid. While all foams containing fluid phases are thermodynamically unstable, their degree of stability or persistence can vary from seconds to weeks. Unstable or low persistence foams, as the name implies, remain for a very short time and collapse as a result of the overwhelming effects of surface tension and gravitational forces. More or less persistent foams can, however, be produced in the presence of extremely small amounts of amphiphilic substances or in the presence of polymers. As little as 5 ppm of saponin, a natural polymeric surfactant extracted from certain trees, in water can produce a foam of finite, though transient, stability.

Metastable foams have a persistence of from a few minutes to months. They are stabilized at the liquid/gas interface by the presence of amphiphilic and/or polymeric materials that retard the loss or drainage of liquid from the area between bubbles, or form a somewhat rigid, mechanically strong bilayer that maintains the foam structure. Because the stabilizing structure of the metastable foams is fluid, it can be disrupted by a number of factors such as vibration, dust particles, evaporation, pressure, and other environmental changes. Even the most stable of the metastable foams must eventually collapse, since the diffusion of gas from smaller to larger bubbles (Ostwald ripening) will occur, regardless of the strength of the interfacial film.

Neither of the first two foam types can be considered to be thermodynamically stable. The third class, the solid foams, could be so considered since they possess a mechanically rigid structure formed as a result of a (presumably) irreversible chemical process during or just after foam formation. Although formulations for the production of solid foams contain additives such as surfactants and blowing agents to produce the foam matrix, their action in sustaining the foam structure is negligible. Such foams therefore are not discussed further.

Foams and emulsions have a great deal in common with regard to the basic physical principles controlling their stability. Some of the equations and concepts presented in this chapter, therefore, will be referred to in the following chapter, although the exact form may change due to the circumstances. The major differences lie in the natures of the dispersed phases (liquid vs. gas), and in the fact that foams will generally involve a much higher volume fraction of dispersed phase than normally is encountered in emulsions. For example, a typical foam (say, angel food cake or ice cream) may have several factors of ten more dispersed phase volume than that of the continuous phase. The ratio of dispersed to continuous phase in an emulsion is unlikely to exceed 3 : 1. The theoretical limit for a monodisperse emulsion of spheres is about 76% dispersed phase although that can

be greater in polydisperse systems. If the dispersed phase is present as deformed spheres or polygons, its content can also exceed the theoretical limit.

When considering the physical and chemical factors involved in the formation and stabilization of foams, it is necessary to look at differences between foaming and non-foaming systems in general. A foam is produced by the introduction of air or other gas into a liquid phase, during which time the bubbles become encapsulated in a film of the liquid. The thin liquid film separating two or more gas bubbles is referred to as a lamellar film, indicating that its nature is related to a layered (laminated) structure that possesses two essentially identical interfaces in close proximity. In the case of a foam of small bubble size, each interface will possess a significant degree of curvature, concave toward the gas phase. The Laplace equation in the form

$$\Delta p = \sigma(1/r_1 + 1/r_2) \quad (11.2)$$

says that there will exist a pressure difference Δp across each interface related to the major radii of curvature of the system, r_1 and r_2 , and the interfacial tension σ . When three or more bubbles are in contact, especially when the foam has reached a more or less stable honeycombed structure, a region will be developed in which the curvature of the lamellae is much greater than that in the main body of the system. These regions, referred to as Plateau borders (Figure 11.1), possess a greater pressure difference than exists elsewhere in the foam. Since the gas pressure within the bubble must be the same throughout, the liquid pressure within the Plateau borders must be lower than in the more parallel areas. As a result, fluid drainage occurs from the lamellar regions into the Plateau borders. Liquid will also be drained from the lamellae because of gravitational forces, and the lamellae will become thinner and thinner; if a critical thickness is reached at which point the system can no longer sustain the pressure, collapse occurs.

The question of foam stability and bubble coalescence requires the consideration of both the static and dynamic aspects of bubble interaction. In the initial stages of film drainage, where relatively thick lamellar films exist between gas bubbles, gravity can make a significant contribution to the drainage of liquid from between foam bubbles. Once the films have thinned to a thickness of a few hundred nanometers, however, gravity effects become negligible, and interfacial interactions begin to predominate. When the two sides of the lamellar film are in sufficiently close proximity, interactions can occur involving the dispersion, electrostatic, and steric forces already discussed in various surfactant contexts. Such forces, acting normal to (across) the lamellar film, make up what is normally referred to as the “disjoining pressure” of the system, $\pi(h)$. The net interaction energy between bubbles as a function of distance of separation through the lamellar phase will have a form similar to that in Figure 11.2, where the minima will correspond to metastable states in which $\pi = 0$ and the films will have some degree of equilibrium stability. In the plane parallel regions of

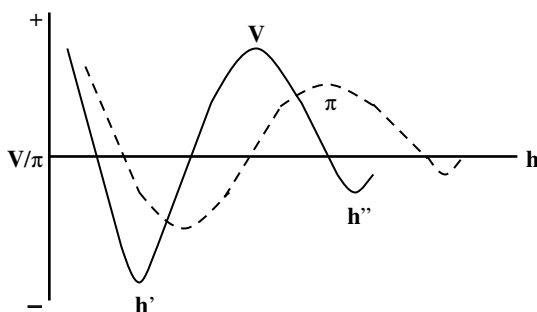


Figure 11.2 Foam bubble interaction energy diagram for total interaction energy (V) between two bubbles and their disjoining pressure (π) as a function of separation distance (h).

the lamellar film, the Laplace (or capillary) pressure given by Eq. (11.2) will be zero. In the Plateau border regions, however, that will not be the case, and mechanical equilibrium requires that

$$\Delta p = -\pi(h) \quad (11.3)$$

Thus, the internal pressure of the bubbles is just balanced by the interfacial forces acting across the lamellar film.

Dynamically, foams may be subjected to any number of environmental stresses that will act to precipitate bubble coalescence and ultimate foam collapse. Regardless of the nature of the stress, however, the ultimate cause of bubble coalescence will always be the same – the loss of liquid from the lamellar layer until a critical thickness of 5–15 nm is reached, and the liquid film can no longer support the pressure of the gas in the bubble. As pointed out above, the loss or drainage of liquid from the lamellae can be affected by a number of factors including (i) a high viscosity in the liquid, which will slow the drainage process and, in some cases, have a dissipating or buffering effect on many types of mechanical disturbances; (ii) surface rheological effects, which can retard the loss of liquid by a viscous drag type of mechanism; and (iii) the presence of repulsive electrical or steric interactions across the lamellae, which can oppose drainage through the effects of the disjoining pressure. The addition of surfactants to a foaming system can alter any or all of these system characteristics and therefore enhance (or reduce) the stability of the foam. Surfactants will also have the effect of lowering the surface tension of the system, thereby reducing the work required for the initial formation of the foam (Eq. (11.1)). With the exception of bulk rheological effects, each of the phenomena relating surfactants to foam formation and stability is discussed in more detail below.

11.2 The Role of Surfactant in Foams

For a liquid to form a foam, it must be able to form a membrane around the gas bubble possessing a form of elasticity that opposes the thinning of the lamellae as a result of drainage. Foaming does not occur in pure liquids because no such mechanism for the retardation of lamellae drainage or interfacial stabilization exists. When amphiphilic materials or polymers are present, however, their adsorption at the gas/liquid interface serves to retard the loss of liquid from the lamellae and, in some instances, to produce a more mechanically stable system. Theories related to such film formation and persistence, especially film elasticity, derive from a number of experimental observations about the surface tension of liquids.

1) As given by the Gibbs adsorption equation,

$$\Gamma_i = \left(-1/RT\right) \left(\delta\sigma_i/\delta \ln a\right)_T \quad (11.4)$$

the surface tension of a solution will decrease as the concentration of the surface-active material in solution increases (assuming positive adsorption) up to its critical micelle concentration (the Gibbs effect).

2) The instantaneous or dynamic surface tension at a newly formed surface is always higher than the equilibrium value; that is, there is a finite time during which the amphiphilic molecules in the bulk solution diffuse to the interface in order to lower the surface tension (the Marangoni effect). The two effects are complementary, often being discussed as the combined Gibbs–Marangoni effect, and they serve as the basis for describing the mechanism of film elasticity under various conditions.

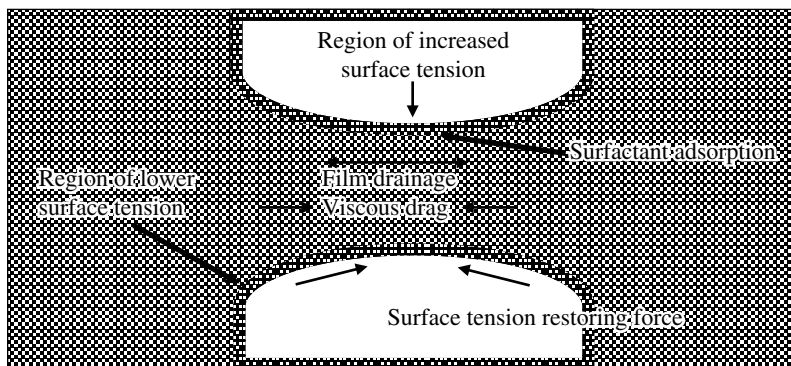


Figure 11.3 Schematic representation of the “healing” action of the Gibbs and Marangoni effects.

It is to be expected, as is observed, that the effects of normal surfactants and polymers or polymeric surfactants can be very time dependent due to the significant differences in the rates of adsorption of the different species at the interface and, in some cases, the time required for specific polymer adsorption phenomena to take place. For example, in a polymer with a range of molecular weight species present, the smaller chains will routinely adsorb first, but they also desorb more readily and are, over time, replaced by the higher molecular weight chains. Such an exchange over time can produce a “ripening” effect in the adsorbed film leading to a more viscous or rigid structure. In systems that contain both monomeric amphiphiles and polymers, the original rapid adsorption of surfactant may be followed by a slow displacement of those species by the adsorption of the polymer.

The fundamental impact of surfactant concentration and diffusion rate in lamellar films can be illustrated as shown in Figure 11.3: as the lamellar film between adjacent bubbles is stretched as a result of gravity, agitation, drainage, etc., new surface is formed at some locations in the film having a lower instantaneous surfactant concentration, and a local surface tension increase occurs. A surface tension gradient along the film is produced, causing liquid to flow from regions of low σ toward the new stretched surface, thereby opposing film thinning. Additional stabilizing action is thought to result from the fact that the diffusion of new surfactant molecules to the surface must also involve the transport of associated solvent into the surface area, again countering the thinning effect of liquid drainage. The mechanism can be characterized as producing a “healing” effect at the site of thinning.

Even though the Gibbs and Marangoni effects are complementary, they are generally important in different surfactant concentration regimes. The Marangoni effect is usually of importance in fairly dilute surfactant solutions and over a relatively narrow concentration range. In the absence of external agitation, the amount of surfactant adsorbed at a new interface can be estimated by the equation

$$n = 2(D/\pi)^{1/2} ct^{1/2} (N/1000) \quad (11.5)$$

where n is the number of molecules per square centimeter, D is the bulk diffusion constant (cm^2/s), c is the bulk concentration of the surfactant (mol/L), t is the time in seconds, and N is Avogadro’s number. Using Eq. (11.5), it is possible to estimate the time required for the adsorption of a given amount of surfactant at a new interface compared with the rate of generation of that interface. If the surfactant solution is too dilute, the surface tension of the solution will not differ sufficiently

Table 11.1 Typical surfactant concentrations required to attain maximum foam height, MFH.

Surfactant	cmc (mM)	Concentration for MFH (mM)
$\text{C}_{12}\text{H}_{25}\text{SO}_3^- \text{Na}^+$	11	13
$\text{C}_{12}\text{H}_{25}\text{OSO}_3^- \text{Na}^+$	9	5
$\text{C}_{14}\text{H}_{29}\text{SO}_3^- \text{K}^+$	3	3
$\text{C}_{14}\text{H}_{29}\text{OSO}_3^- \text{Na}^+$	2.3	3
$\text{C}_{16}\text{H}_{33}\text{SO}_3^- \text{K}^+$	0.9	0.8
$\text{C}_{16}\text{H}_{33}\text{OSO}_3^- \text{Na}^+$	0.7	0.8
$p\text{-C}_8\text{H}_{17}\text{C}_6\text{H}_4\text{SO}_3^- \text{Na}^+$	16	13
$p\text{-C}_{10}\text{H}_{21}\text{C}_6\text{H}_4\text{SO}_3^- \text{Na}^+$	3	4.5
$p\text{-C}_{12}\text{H}_{25}\text{C}_6\text{H}_4\text{SO}_3^- \text{Na}^+$	1.2	4
$o\text{-C}_{12}\text{H}_{25}\text{C}_6\text{H}_4\text{SO}_3^- \text{Na}^+$	3	4
$(\text{C}_8\text{H}_{17})_2\text{CHSO}_4^- \text{Na}^+$	2.3	4

from that of the pure solvent for the restoring force to counteract the effects of thermal and mechanical agitation. As a result, the foam produced will be very transient. In line with the Marangoni theory, there should be an optimum surfactant concentration for producing the maximum amount of foam in a given system, under defined circumstances. Such effects have been verified experimentally (see Table 11.1).

In the case of the Gibbs effect, the increase in surface tension occurring as the film is stretched results from a local depletion of the surfactant concentration in the bulk phase just below the newly formed interface. Obviously, in systems such as foams where the available bulk phase in the narrow lamellae may be small compared with the amount of interface being formed, the effect will be enhanced. As with the Marangoni effect, if the surfactant concentration in the bulk phase is too low, a surface tension gradient of sufficient size to produce the necessary “healing” action will not be produced. Conversely, if the concentration is too large, well above the **cmc**, the amount of “immediately” available surfactant will be such that no gradient is formed.

Quantitatively, the Gibbs effect can be described in terms of a coefficient of surface elasticity **E**, which is defined as the ratio of the surface stress to the strain per unit area

$$\mathbf{E} = 2\mathbf{A}(\delta\sigma/\delta\mathbf{A}) \quad (11.6)$$

where **A** is total surface or interfacial area and σ is surface tension. Since the elasticity is the resistance of the film to deformation, the larger the value of **E**, the greater will be the ability of the film to resist mechanical shocks without rupture. As mentioned earlier, when a film of a pure liquid is stretched, no significant change in surface tension will occur, and the elasticity as defined by Eq. (11.6) will be zero. This is the theoretical basis for the observation that pure liquids will not foam.

In addition to the Gibbs and Marangoni effects, foam stability can also be affected by surface and bulk solution transport phenomena. The surface tension gradients induced by the stretching of a film will result in the flow of liquid from a region of low to one of high surface tension. Since the movement of molecules in a liquid is never independent of adjacent molecules, such surface flow will result in the transport of bulk solution beneath the surface in the same direction; that is,

underlying solution will be dragged in the same direction as, but to a smaller extent than, the surface layer itself.

The relationship between surface elasticity and surface transport is important since, if a film has a significant value of $E > 0$, stretching the film will produce an increase in the local surface tension and induce flow of bulk liquid into the stretched area, acting to restore the original thickness of the lamellae. Two surfactant solution processes must be considered in conjunction with these foam-stabilizing mechanisms. One is the rate of surface diffusion of surfactant molecules from regions of low to those of high surface tension. The second is the rate of adsorption of surfactant from the underlying bulk phase into the surface. In each case, a too rapid arrival of surfactant molecules at the new surface will destroy the surface tension gradient and prevent the restoring action of the Gibbs–Marangoni “healing” process.

11.2.1 Foam Formation and Surfactant Structure

The relationship between the foaming power of a surfactant and its chemical structure is, as is the case for most surfactant applications, quite complex. The correlation of structure and foaming ability is further complicated by the fact that there is not necessarily a direct relationship between the ability of a given structure to produce foam and its ability to sustain that foam. It is generally found that the amount of foam produced by a surfactant under a given set of circumstances will increase with its bulk concentration up to a maximum, which occurs somewhere near the **cmc**. It appears, then, that surfactant **cmc** can be used as a guide in predicting the foaming ability of a material, but not necessarily the persistence of such foams. Any structural modification that leads to a lowering of the **cmc** of a particular class of surfactants, such as increasing the chain length of an alkyl sulfate, can be expected to increase its efficiency as a foaming agent. Conversely, branching of the hydrophobic chain or moving the hydrophilic group to an internal position, all of which increase the **cmc**, will usually result in a lower foaming efficiency. Typical foaming characteristics for several anionic and nonionic surfactants are given in Table 11.2, where foaming efficiency and persistence were determined according to the industry standard Ross–Miles procedure.

The ability of a surfactant to perform as a foaming agent is dependent primarily on its effectiveness at reducing the surface tension of the solution, its diffusion characteristics, its properties with regard to disjoining pressures in thin films, and the elastic properties it imparts to interfaces. The amount of foam that can be produced in a solution under given conditions (i.e. for a set amount of work input) will be related to the product of the surface tension and the new surface area generated during the foaming process (Eq. (11.1)). Obviously, the lower the surface tension of the solution, the greater will be the surface area that can be expected to be developed by the input of a given amount of work. The amount of foam produced by a surfactant solution is only one part of the foaming story, however. Maintenance of the foam may be as important as original formation.

It is often observed that the amount of foam produced by the members of a homologous series of surfactants will go through a maximum as the chain length of the hydrophobic group increases. This is probably due to the conflicting effects of the structural changes. In one case, a longer-chain hydrophobe will result in a lower **cmc** and a more rapid lowering of surface tension. However, if the chain length grows too long, low solubility and slow diffusion may become a problem.

It has been found in many instances that surfactants with branched hydrophobic groups will lower the surface tension of a solution more rapidly than a straight-chain material of equal carbon number. However, since the branching of the chain increases the **cmc** and reduces the amount of lateral chain interaction and the associated surface viscosity, the cohesive strength of the adsorbed layer and the film elasticity will be reduced, yielding a system with higher initial foam height but

Table 11.2 Foaming characteristics of typical anionic and nonionic surfactants in distilled water (Ross–Miles, at 60 °C).

Surfactant	Concentration (wt. %)	Foam height	
		Initial	After (minutes)
$\text{C}_{12}\text{H}_{25}\text{SO}_3^- \text{Na}^+$	0.25	225	205(1)
$\text{C}_{12}\text{H}_{25}\text{OSO}_3^- \text{Na}^+$	0.25	220	175(5)
$\text{C}_{14}\text{H}_{29}\text{SO}_3^- \text{Na}^+$	0.11	240	214(1)
$\text{C}_{14}\text{H}_{29}\text{OSO}_3^- \text{Na}^+$	0.25	231	184(5)
$\text{C}_{16}\text{H}_{33}\text{SO}_3^- \text{K}^+$	0.033	245	233(1)
$\text{C}_{16}\text{H}_{33}\text{SO}_3^- \text{Na}^+$	0.25	245	240(5)
$\text{C}_{18}\text{H}_{37}\text{OSO}_3^- \text{Na}^+$	0.25	227	227(5)
$o\text{-C}_8\text{H}_{17}\text{C}_6\text{H}_4\text{SO}_3^- \text{Na}^+$	0.15	148	—
$p\text{-C}_8\text{H}_{17}\text{C}_6\text{H}_4\text{SO}_3^- \text{Na}^+$	0.15	134	—
$o\text{-C}_{12}\text{H}_{25}\text{C}_6\text{H}_4\text{SO}_3^- \text{Na}^+$	0.25	208	—
$t\text{-C}_9\text{H}_{19}\text{C}_6\text{H}_4\text{O}(\text{CH}_2\text{CH}_2\text{O})_8\text{H}$	0.10	55	45(5)
$t\text{-C}_9\text{H}_{19}\text{C}_6\text{H}_4\text{O}(\text{CH}_2\text{CH}_2\text{O})_9\text{H}$	0.10	80	60(5)
$t\text{-C}_9\text{H}_{19}\text{C}_6\text{H}_4\text{O}(\text{CH}_2\text{CH}_2\text{O})_9\text{H}$	0.10	110	80(5)
$t\text{-C}_9\text{H}_{19}\text{C}_6\text{H}_4\text{O}(\text{CH}_2\text{CH}_2\text{O})_{13}\text{H}$	0.10	130	110(5)
$t\text{-C}_9\text{H}_{19}\text{C}_6\text{H}_4\text{O}(\text{CH}_2\text{CH}_2\text{O})_{20}\text{H}$	0.10	120	110(5)

reduced foam stability. Similarly, if the hydrophilic group is moved from a terminal to an internal position along the chain, higher foam heights, but lower persistence, can be expected. In all such cases, comparison of foaming abilities must be made at concentrations above their **cmc**'s.

Ionic surfactants can contribute to foam formation and stabilization as a result of the presence at the interface of an electrical double layer that can interact with the opposing interface in the form of the disjoining pressure. Additional stabilizing effect may be gained because of the requirement of the ionic group for a significant number of bound solvent molecules that will contribute to the steric (or entropic) contribution to the disjoining pressure. Not surprisingly, it is found that the foaming effectiveness of such surfactants can be related to the nature of the counterion associated with the surfactant. It is found, for example, that the effectiveness of a series of dodecyl sulfate surfactants with ammonium counterions as foam stabilizers decreases in the order $\text{NH}_4^+ > (\text{CH}_3)_4\text{N}^+ > (\text{C}_2\text{H}_5)_4\text{N}^+ > (\text{C}_4\text{H}_9)_4\text{N}^+$. Such an order may reflect changes in the solvation state of the surfactant from highly dissociated (ammonium) to a more tightly ion-paired system (tetrabutylammonium).

Nonionic surfactants generally produce less initial foam and less stable foams than ionic in aqueous solution. Because such materials must, by nature of their solvation mechanism, have rather large surface areas per molecule, it becomes difficult for the adsorbed molecules to interact laterally to a significant degree, resulting in a lower interfacial elasticity. In addition, the bulky, highly solvated nonionic groups will generally result in lower diffusion rates and less efficient “healing” via the Gibbs–Marangoni effect. POE nonionic surfactants in particular exhibit a strong sensitivity of foaming ability to the length of the hydrophilic chain. At short-chain lengths, the material may not have sufficient water solubility to lower the surface tension and produce foam. A chain that is

too long, on the other hand, will greatly expand the surface area required to accommodate the adsorbed molecules and will also reduce the interfacial elasticity. This characteristic of POE non-ionic surfactants has made it possible to design highly surface active yet low foaming surfactant formulations. Even more dramatic effects can be obtained by the use of “double-ended” surfactants in which both ends of the POE chain are substituted. In many cases, substitution of a methyl group on the end of a surfactant chain will significantly reduce foaming in materials with the same primary hydrophobic group and POE chain length.

If the solubility of a surfactant is highly temperature dependent, its foaming ability will generally increase in step with its solubility. Nonionic POE surfactants, for example, exhibit a decrease in foam production as the temperature is increased and the cloud point is approached. Long-chain carboxylate salts, on the other hand, which may have limited solubility in water and poor foaming properties at room temperature, will be more soluble and will foam more as the temperature increases.

Quantitatively, the foaming abilities of some surfactants have been correlated with their Hildebrand or Hansen solubility parameters (see Bibliography), which is a semiquantitative, thermodynamically based molecular cohesion parameter that provides a simple method for predicting and correlating the cohesive and adhesive properties of materials based on knowledge of their constituent parts. Although less has been published in relation to foaming in this area than in the areas of polymer solubility and miscibility or emulsions, it remains a potentially interesting approach for investigating structure–property relationships between surfactant structures and their activity in foam systems. Since foaming can be related to the solubility of the surfactant (too high a solubility results in low adsorption; too low, in insufficient availability of surfactant molecules), it is reasonable to expect that reasonably good correlations can be made between surfactant structure and foaming ability using Hansen parameters or related cohesive energy density approaches.

11.2.2 Amphiphilic Mesophases and Foam Stability

As we have seen, the stability of foams depends on a wide variety of factors involving several aspects of surface science. The potential importance of mesophase formation to the stability of emulsions and foams was briefly mentioned in Chapter 7. Although the phenomenon of mesophase stabilization of aqueous foams has been recognized for some time, the role of such phases in nonaqueous foaming systems has been less well documented. However, since nonaqueous systems lack the advantages of electrostatic interactions in most aspects of their surface and colloid chemistry, it is not surprising to find that the presence of mesophase can serve as a sufficient condition for the production of stable foams in organic systems.

The role of mesophases in stabilizing a foam can be related to their effects on several mechanisms involved in foam collapse, including film drainage and the mechanical strength of the liquid film.

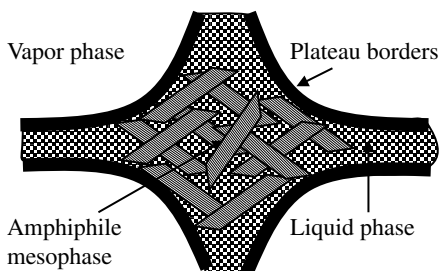


Figure 11.4 A schematic representation of the possible role of amphiphile mesophases in the stabilization of foams.

The effect of mesophases on film drainage can be considered to be twofold. In the first place, the more extended and ordered nature of the mesophases imparts a higher viscosity to the film than a normal surfactant monolayer. A simple-minded physical picture of the potential extent of mesophase penetration into the liquid lamellar phase would intuitively suggest that they should significantly affect the flow and drainage of liquid from between the two monolayers making up the bilayer film (Figure 11.4). It might also

be expected that the sheer physical interaction between neighboring mesophase units would impart mechanical rigidity to the system. In addition, it has been shown that mesophases tend to accumulate in the Plateau border areas. Their presence there results in an increase in the size of the areas, a larger radius of curvature, and thus a smaller Laplace pressure. The second stabilizing function of the mesophases can be related to the Gibbs–Marangoni effects, in that the presence of a large quantity of surfactant at the Plateau borders allows them to act as a reservoir for surfactant molecules needed to maintain the high surface pressures useful for ensuring foam stability.

Obviously, the presence of mesophases or other structures such as mixed surfactant complexes, not only can increase the stability of the foam from a surface chemical standpoint but also can significantly enhance the physical strength of the system. When thinning reaches the point at which bubble rupture becomes important, the mechanical strength and rigidity of such structures might help the system withstand the thermal and mechanical agitation that would otherwise result in film failure and foam collapse.

11.2.3 The Effects of Additives on Surfactant Foaming Properties

As we have seen, the foaming properties of a surfactant can be related to its solution properties through the **cmc**. It is not surprising, then, that additives in a formulation can affect foaming properties in much the same way that they affect other solution properties. The presence of additives can affect the stability of a foam by influencing any of the mechanisms already discussed for foam stabilization. It may, for example, increase the viscosity of the liquid phase or the interfacial layer, or it may alter the interfacial interactions related to Gibbs–Marangoni effects or electrostatic repulsions. By the proper choice of additive, a normally low foaming material may produce large amounts of foam in the presence of small amounts of another surface-active material, which itself has few if any useful surfactant properties. Conversely, a high foaming surfactant can be transformed into one exhibiting little or no foam formation by the judicious (or accidental) addition of the right (or wrong) additive. It is theoretically possible, then, to custom-build a surfactant formulation to achieve the best desirable combination of surfactant actions to suit the individual needs of the system. The use of small amounts of such additives has become the primary way of adjusting the foaming characteristics of a formulation in many practical surfactant applications.

As mentioned earlier, additives that alter the micellization of a surfactant will also affect its foaming properties. Such additives can be divided into three main classes: (i) inorganic electrolytes, which are most effective with ionic surfactants; (ii) polar organic additives, which can affect surfactants of all types; and (iii) macromolecular materials, which can affect the foaming properties of a system in many ways, some unrelated to the surface properties of the surfactant itself.

It was shown in Chapter 6 that the **cmc** of ionic surfactants can be very sensitive to the presence of electrolytes in the solution. It should not be surprising to find, then, that their presence also increases the foaming ability of such surfactants, within limits. The addition of excess monovalent ions to an ionic surfactant solution will, as expected, lower the **cmc** and improve the foaming ability of the amphiphilic material, although that improvement may not be particularly spectacular. If di- and trivalent ions are added in significant amounts to an anionic surfactant system, solubility problems may arise, reducing the foaming characteristics of the system considerably. On the other hand, such ions may enhance the foaming effectiveness of the surfactant in nonaqueous solvent systems. As a general rule of thumb, it can be assumed (or guessed) that any ionic additive that decreases the **cmc** of an ionic surfactant will increase its effectiveness as a foaming agent.

From a practical standpoint, perhaps the most important class of additives to enhance foaming is that of the polar organic materials, and they have received a corresponding amount of attention

Table 11.3 The effect of organic additives on the **cmc** and foaming characteristics of sodium 2-*n*-dodecylbenzene sulfonate solutions.

Additive	cmc (g/L)	cmc (%)	Foam volume (mL at 2 minutes)
None	0.59		18
Lauryl glycerol ether	0.29	−51	32
Laurylethanolamide	0.31	−48	50
<i>n</i> -Decyl glycerol ether	0.33	−44	34
Laurylsulfolanylamide	0.35	−41	40
<i>n</i> -Octylglycerol ether	0.36	−39	32
<i>n</i> -Decyl alcohol	0.41	−31	26
Caprylamide	0.50	−15	17
Tetradecanol	0.60	0	12

both academically and industrially. In the search for foam stabilizers for heavy-duty laundry formulations, investigators found that organic additives that lower the **cmc** of a surfactant could stabilize foams in the presence of materials that were normally detrimental to foam formation and persistence. Results indicated that increases in foaming and foam persistence induced by the additives could be related directly to the extent to which the material lowered the **cmc** of the surfactant. Straight-chain hydrocarbon additives with chain lengths approximately the same as that of the surfactant were the most effective at lowering the **cmc** and increasing foam height. Bulky chains on the additives produced much smaller effects. The effectiveness of polar additives of various types as foam stabilizers was found to be in the approximate order: *N*-substituted amides > amides > sulfonyl ethers > glyceryl ethers > primary alcohols. This is essentially the same order found for the effects of such materials on the **cmc** of surfactants. Typical data showing the effects of polar additives on the **cmc** and foam persistence of sodium dodecylbenzene sulfonate solutions are given in Table 11.3. A quick glance at the ingredients list of almost all shampoos will indicate the presence of long-chain hydrocarbon amides to produce copious foam, perhaps more for esthetic reasons than for enhancing the cleaning ability of the product.

Not only does foam stabilization by polar organic additives seem to go hand in hand with the effect of the additive on the **cmc** of the surfactant, but also there is a correlation with the relative amount of additive that is located in the interfacial film. The greater the mole fraction of additive adsorbed at the interface, the more stable is the resulting foam. Many of the most stable foaming systems were found to have surface layers composed of as much as 60–90 mol % additive.

Considering the mechanisms of foam stabilization mentioned above, it is not surprising to find that the addition of polymers to a surfactant solution will often enhance the foaming effectiveness of the system. In such systems, the added polymer may or may not affect the **cmc** of the surfactant, but it will undoubtedly affect the rheology of the liquid phase. Since foam production is usually a rapid, high-energy input process, new surface area is produced rapidly, and the surfactant molecules must diffuse rapidly to that new interface. A typical water-soluble polymer will diffuse too slowly to be effective in foam formation, the great exceptions being polymers that are themselves surface active such as proteins and other structures mentioned in Chapter 9. If the polymer additive does not contribute to initial foam formation, the increased solution viscosity in the lamellar film of the foam will naturally retard drainage and therefore enhance foam persistence. If the

polymer can, over time, displace adsorbed surfactant from the air–liquid interface, the added interfacial viscosity and monolayer rigidity will normally add to the stability of the foam.

If polyelectrolytes are employed, the addition of di- and trivalent ions such as calcium and aluminum may produce particularly rigid and stable foams. The foam is desirable, that is, all well and good. In systems where foaming is not desirable, however, such effects can significantly complicate life. In wastewater treatment plants, for example, the combination of proteins and metal ions such as Al^{3+} can produce particularly troublesome foams that can almost shut a system down.

11.3 Foam Inhibition

Although the presence of some additives can enhance the foaming effectiveness and persistence of a surfactant system, the properly chosen materials can also reduce or eliminate foams. Such materials are termed foam inhibitors, if they act to prevent the formation of foam, or foam breakers, if they increase the rate of foam collapse. Foam breakers may include inorganic ions such as calcium, which counteract the effects of electrostatic stabilization or reduce the solubility of many ionic surfactants, or organic or silicone materials that act by spreading on the interface and displacing the stabilizing surfactant species.

A foam breaker that acts by spreading may do so by adsorption as a monolayer, displacing the surfactant molecules that would normally assist in foam formation and stabilization, or as a lens, accumulating in spots along the interface and leaving “weak spots” that can be easily ruptured by mechanical or gravitational forces (Figure 11.5). In addition, such defects in the lamellar walls will not normally be subject to the healing Gibbs–Marangoni effects. In either case, it is assumed that the spreading foam breaker sweeps away the stabilizing layer, leading to rapid bubble collapse. The rate of spreading of the defoamer will, of course, depend on the nature of the adsorbed layer present initially. If the surfactant can be easily displaced from the interface, the defoamer will spread rapidly, resulting in fast foam collapse, or essentially no notable foam formation. If the surfactant

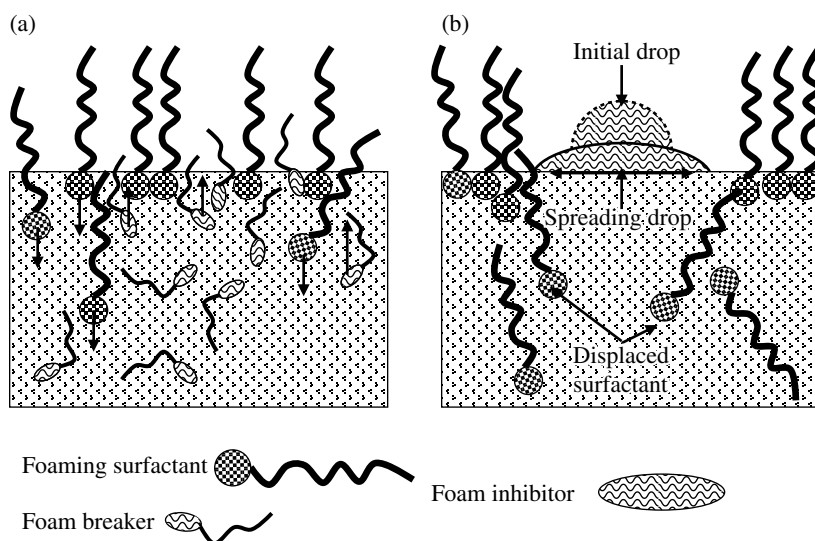


Figure 11.5 Mechanisms of foam breaking: (a) surfactant displacement (monomolecular film) and (b) lens formation.

is not displaced rapidly, on the other hand, spreading will be retarded, or even halted. Foam collapse will then be a much slower process relying on the thinning or weakening of the lamellae by other drainage mechanisms.

Studies of the relationship between the action of defoamers and the concentration of the surfactant found that if the surfactant concentration was below the **cmc**, the defoamer was most effective if it spread as a lens on the surface rather than as a monolayer film. That is, the defoamer produced a defective lamellar structure that could not withstand the mechanical rigors of the foaming process for sufficient time for the normal stabilizing mechanisms to take hold. In the presence of micelles, the defoamer may be solubilized in the micelles, which can act as a reservoir for extended defoaming action by adsorption as a surface monolayer. When the solubilization limit was reached, additional defoaming effect was obtained by the lens spreading mechanism.

So far, the discussion of foams and defoaming has centered on aqueous systems. While most organic liquids will do not form stable foams, the presence of polymers and oil-soluble amphiphiles can result in persistent foams, whether wanted or unwanted.

A classical and commonly encountered example of unwanted foaming in organic liquids is that of used frying oil. While a fresh vegetable oil or fat will not form foam, the frying process brings about several chemical changes that result in foaming systems. One effect is that the components of the material being fried, especially water, will slowly bring about saponification of the oil to produce free fatty acids and mono-diglycerides in the system. Both materials are amphiphilic, of course. If neutralization of the fatty acids occurs, soap is formed. A second effect of the frying process is oxidation of the unsaturated fatty acid chains. At frying temperatures, the polyunsaturated acids such as linoleic and linolenic are particularly susceptible to oxidation, introducing peroxide and hydroxyl groups that enhance the amphiphilic character of the materials with the observed result. Such reactions also produce unwanted flavor changes in the fried product, of course. For those reasons, among others, frying oils have limited useful lifetimes and are often stabilized by the addition of antioxidants.

Another basically nonaqueous system that tends to produce unwanted foam is that of lubricating oils. Many such products contain amphiphilic materials for the purposes of reducing friction and corrosion control. However, since the oil is recycled, the presence of foam can foul the recycling mechanism. It has been found that silicone fluids, some of the few materials having the required characteristics of limited solubility and adequate surface tension lowering in organic liquids, act as foaming agents below their solubility limit but inhibited foam formation when that limit was exceeded.

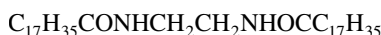
11.4 Chemical Structures of Antifoaming Agents

Materials that are effective as antifoaming or defoaming agents can be classified into eight general chemical classifications, with the best choice of material depending on such factors as cost, the nature of the liquid phase, and the nature of the foaming agent present. One of the most common classes of antifoaming agents is polar organic materials such as highly branched aliphatic alcohols. As noted earlier, linear alcohols, in conjunction with surfactants, can increase foam production and stability due to mixed monolayer formation and enhanced film strength. The branched materials, on the other hand, reduce the lateral cohesive strength of the interfacial film, which increases the rate of bubble collapse. The higher alcohols also have limited water solubility and are strongly adsorbed at the air–water interface, displacing surfactant molecules in the process.

Fatty acids and esters with limited water solubility are also often used as foam inhibitors. Their mode of action is similar to that of the analogous alcohols. In addition, their generally low toxicity

often makes them attractive for use in food applications. If the acids are neutralized to soaps, however, their antifoaming usefulness disappears. Organic compounds with multiple polar groups are, in general, found to be effective foam inhibitors. The presence of several polar groups generally acts to increase the surface area per molecule of the adsorbed antifoaming material and results in a loss of stabilization.

Metallic soaps of carboxylic acids, especially the water-insoluble polyvalent salts such as calcium, magnesium, and aluminum, can be effective as defoamers in both aqueous and nonaqueous systems. In water, they are usually employed as solutions in an organic solvent, or as a fine dispersion in the aqueous phase. Water-insoluble organics containing one or more amide groups are found to be effective antifoaming agents in a number of applications, especially for use in boiler systems. It is generally found that greater effectiveness is obtained with materials containing at least 36 carbon atoms compared with simple fatty acid amides. An example of such a material would be distearoylethylenediamine:



Alkyl phosphate esters are found to possess good antifoaming characteristics in many systems because of their low water solubility and large spreading coefficient. They also find wide application in nonaqueous systems such as inks and adhesives. Organic silicone compounds are also usually found to be outstanding antifoaming agents in both aqueous and organic systems. Because of their inherently low surface energy and limited solubility in many organics, the silicone materials constitute one of the two types of material that are available to modify the surface properties of most organic liquids.

The final class of materials that have found some application as antifoaming agents are the fluorinated alcohols and acids, which are related to those discussed earlier. As a result of their very low surface energies, they are active in liquids where the hydrocarbon materials have no effect.

11.5 A Summary of the Foaming and Antifoaming Activity of Additives

As pointed out above, the mechanisms of action of foaming and antifoaming materials are quite often, understandably, opposite in nature. Foam stabilizers, for example, may increase the surface viscosity, leading to slower liquid drainage and lower gas permeability, or they may lower the critical micelle concentration of the primary foaming agent. They may also enhance the “healing” effects related to surface elasticity and the Gibbs–Marangoni effect. Antifoaming agents, on the other hand, may decrease surface viscosity and elasticity by displacing or disrupting the structure formed by adsorbed surfactant molecules. In addition, they can retard micelle formation and otherwise alter the surfactant properties of the system.

There are, however, similarities between the two types of material in that each usually has limited solubility in the aqueous liquid phase and each can produce a lowering of the surface tension of the system beyond that produced by the primary surfactant. However, the concentration levels at which the two are most effective differ. The antifoaming agents, for example, perform best when present at levels in excess of their solubility limit, being held in reserve by solubilization in micelles. Foam stabilizers, however, are most effective when completely dissolved and may, in fact, become antifoaming agents when present as a separate phase.

As noted earlier, antifoaming agents may act as a result of spreading over the foam surface. In such cases the film elasticity becomes essentially zero (as a lens), or they produce a surface film that provides little opposition to film drainage (as a monolayer). They are rapidly adsorbed at new interfaces so that the surface tension gradients necessary for the “healing” action of the Gibbs and Marangoni effects cannot develop.

It is often found that foam stabilizers can increase the solubility of antifoaming agents by increasing their solubilization in micelles. There is a sort of competition between the foam stabilizer trying to keep the antifoaming agent at bay while the surfactant does its job and the antifoaming material trying to prevent the surfactant from doing just that.

11.6 The Spreading Coefficient

Foaming agents can also prevent or retard the spreading of the antifoaming agents at the interface by lowering the liquid surface tension and producing an unfavorable spreading coefficient, $S_{2/1}^\sigma$, given by

$$S_{2/1}^\sigma = \sigma_1 - \sigma_2 - \sigma_{12} \quad (11.7)$$

where σ_1 and σ_2 are the surface tensions of the liquid substrate and spreading liquid, respectively, and σ_{12} is the interfacial tension between the two.

The spreading coefficient is a measure of the free energy change for the spreading of liquid 2 over the surface (solid or liquid) 1 and is called the spreading coefficient of 2 on 1, $S_{2/1}^\sigma$. Essentially, $S_{2/1}^\sigma$ is the difference between the thermodynamic work of adhesion of 2 to 1 and the work of cohesion of 2. In this context, the term “adhesion” refers to the interaction of two different materials and “cohesion” that of a material with itself. From Eq. (11.7), it is clear that $S_{2/1}^\sigma$ will be positive if there is a decrease in free energy on spreading (i.e. adhesive forces dominate), and the spreading process will be spontaneous. If $S_{2/1}^\sigma$ is negative, then cohesive forces will dominate, and a drop or lens will result. What Eq. (11.7) also says is that when a liquid of low surface tension such as a hydrocarbon is placed on a liquid or solid of high surface energy such as clean glass or mercury, spontaneous spreading occurs. Conversely, if a liquid of high surface tension such as water is placed on a surface of lower surface energy such as Teflon or paraffin wax, drop or lens formation results.

Unfortunately, complications arise in spreading phenomena due to the fact that liquids, solids, and gases tend to interact in bulk processes as well as at interfaces, and those bulk-phase interactions may have significant effects on interfacial phenomena. In particular, gases tend to adsorb at solid interfaces and change the free energy of those surfaces, σ_{SV} ; they may also become dissolved in liquid phases and thereby alter the liquid surface tension. More importantly, liquids in contact with other liquids tend to become mutually saturated, meaning that the composition of the two phases may not remain “pure” and no longer have the surface characteristics of the original materials. Finally, liquids and solutes, like gases, can adsorb at solid interfaces to alter the surface characteristics of the solid and thereby change the thermodynamics of the spreading process. A classic example of the effects of such complications is that of the benzene–water system.

For a drop of pure benzene ($\sigma_2 = 28.9 \text{ mN/m}$) placed on a surface of pure water ($\sigma_1 = 72.8 \text{ mN/m}$) with an interfacial tension, σ_{12} of 35.0 mN/m , Eq. (11.7) predicts a spreading coefficient of

$$S_{2/1}^\sigma = 72.8 - 28.9 - 35.0 = 8.9 \text{ mN/m}$$

The positive spreading coefficient indicates that benzene should spread spontaneously on water. When the experiment is carried out, it is found that after an initial rapid spreading, the benzene layer will retract and form a lens on the water. How can this seemingly anomalous result be explained?

In this and many similar cases, it must be remembered that benzene and many other liquids of low water miscibility have, in fact, a small but finite solubility and the water will rapidly become saturated with benzene. Benzene, having a lower surface tension than water, will adsorb at the water–air interface so that the surface will no longer be that of pure water but that of water with a surface excess of benzene. The surface tension of benzene-saturated water can be measured and is found to be 62.2 mN/m, which is now the value that must be used to calculate the spreading coefficient instead of that for pure water, so that

$$S_{2/1(2)}^\sigma = 62.2 - 28.9 - 35.0 = -1.7$$

where the subscript 1(2) indicates phase 1 saturated with phase 2. The negative spreading coefficient indicates that lens formation should occur, as is observed. The saturation process occurs, of course, in both phases. However, since water is a material of relatively high surface tension, it will have little tendency to adsorb at the benzene–air interface and will therefore cause little change in the surface tension of the benzene. In this case $\sigma_{2(1)} = 28.8$ mN/m so that

$$S_{B(A)/A}^\sigma = 72.8 - 28.8 - 35.0 = 9.0$$

If only the benzene layer were affected by the saturation process, spreading would still occur. Combining the two effects one obtains

$$S_{2(1)/1(2)}^\sigma = 62.2 - 28.8 - 35.0 = -1.6$$

indicating that it is the effect of benzene in water that controls the spreading (or non-spreading) in this system. The interfacial tension of water–benzene is unchanged throughout because it inherently includes the mutual saturation process.

Situations like that for benzene are very general for low surface tension liquids on water. There may be initial spreading followed by retraction and lens formation. A similar effect can in principle be achieved if a third component (e.g. a surfactant) that strongly adsorbs at the water–air interface, but not the oil–water interface, is added to the system. Conversely, if the material is strongly adsorbed at the oil–water interface, lowering the interfacial tension, spreading may be achieved where it did not occur otherwise. This is, of course, a technologically very important process and will be discussed in more detail in Chapters 12 and 13.

For normal use, it is assumed that the values of σ represent equilibrium saturation values. The antifoaming materials reduce the strength of the surface film by reducing the lateral van der Waals interactions between adsorbed molecules due to branching in the hydrophobic tail. They may also be made to lie flat in the surface by the inclusion of several hydrophilic groups along the chain, by placing the hydrophile in the middle of the chain, and by using the smallest number of methylene groups in the chain consistent with the necessity for limited solubility.

In summary, it can be said that the various aspects of foam formation and persistence are related to the actions of surfactant molecules and additives at the various interfaces in the system, coupled with the rheological characteristics of the system, including the dilational viscosity of the

interfacial layers and the bulk rheological properties of the system. Depending on whether foam is wanted or not, the choice of surfactants and additives for a formulation must address all of those factors in the context of the system being prepared and its end use.

11.7 Liquid Aerosols

Mists and fogs are colloidal dispersions of a liquid in a gas. They may therefore be thought of as being the inverse of foams. The interactions controlling their stability, however, are not generally the same as those involved in foam stabilization, because most mists and fogs do not possess the thin lamellar stabilizing films encountered in foams. In fact, the stability of liquid aerosols is usually more dependent on fluid dynamics than on colloidal factors, as illustrated below.

11.7.1 The Formation of Liquid Aerosols

Liquid aerosols may be formed by one of two processes, depending on whether the dispersed system begins as a liquid or undergoes a phase change from vapor to liquid during the formation process. In the first case, since the dispersed material does not change phases, the aerosol is formed by some process that reduces the particle size of the liquid units. To this class belong spray mists such as those formed at the bottom of a waterfall or by ocean waves (impact), mists produced by vigorous agitation (mechanical breakup), and those formed by some direct spraying or atomization process. Liquid aerosols can also be formed directly by the application of high electrical potentials to the liquid. The second class of mists or fogs is that produced by some process in which the incipient liquid phase is introduced as a vapor and forms droplets as a result of some equilibrium condensation process or the liquid is produced as a result of some chemical reaction. The former mechanism includes, of course, cloud and fog formations, while the latter corresponds to some “chemical” fogs and mists.

11.7.1.1 Spraying and Related Mechanisms of Mist and Fog Formation

Liquid aerosol formation by spraying is a very important industrial process, even though some of the fundamental details of the process are still not very well understood. Major applications include paint application; fuel injection in diesel, gasoline, and jet engines; spray drying of milk, eggs, etc.; the production of metal and plastic powders (spray cooling); medicinal nose and throat sprays; the application of pesticides to crops; and many more. In all of those applications, it is vitally important that the characteristics of the aerosol produced be optimized to produce the desired particle size and dispersion. Theories related to the formation of drops in spray systems can be very helpful in approximating the conditions necessary to produce an aerosol of defined characteristics. However, because of the nature of the process and the incidence of hard to control external factors, it is usually necessary to arrive at the optimum spraying system by trial-and-error techniques based on previous experience in the field.

Aerosol sprays may be formed mechanically by one of four basic processes as illustrated in Figure 11.6. These include the following:

- 1) Directing a jet of liquid against a solid surface thereby breaking the liquid up into fine droplets.
- 2) Ejecting a jet of liquid from an orifice into a stream of air or gas.
- 3) Ejecting a stream of liquid from a small orifice under high pressure.
- 4) Dropping liquid onto a solid rotating surface from which small droplets are ejected by centrifugal force.

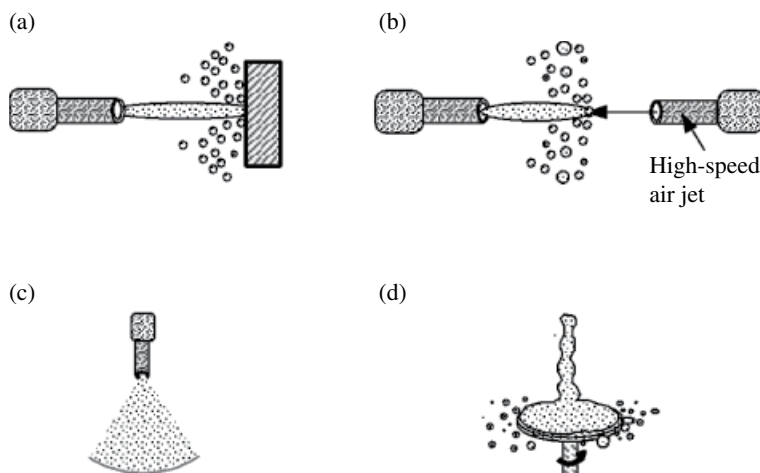


Figure 11.6 Mechanical processes for liquid aerosol formation (a) surface impact of a high-pressure liquid stream, (b) air jet impact the collision of high-velocity liquid and gas streams, (c) high-pressure spray nozzles, and (d) spinning disk centrifugal atomizers.

Other systems exist but are of much less significance in practice. Of the four, the most important industrially are the high-pressure orifice or nozzle sprays and some variation of the rotating disk. For that reason, they will be discussed briefly below.

Although the production of aerosols by spray techniques is of great practical importance, the physics of the processes are still not completely understood. Numerous attempts have been and are being made to quantify and understand the phenomena involved in order to get a better practical handle on the matter. Most of those treatments are quite complex and beyond the scope of this book. However, it may be instructive to work through two relatively simple approaches in order to see how surface tension forces and, by association surfactants, can come into play.

Spray production by methods involving high-speed ejection of a liquid through an orifice (nozzle atomization) and ejection from a spinning disk by centrifugal force (rotary atomization) are the simplest and most important situations because they require knowledge of only one material velocity – that of the liquid. Spray production by the action of an incident air stream on a jet of liquid involves, of course, the velocity of both the liquid and the air.

11.7.1.2 Nozzle Atomization

If a liquid is forced through an orifice (nozzle) under a pressure, the velocity of the liquid in the channel of the orifice becomes so high that turbulent flow is encountered. That is, the liquid will not flow smoothly in lines parallel to the walls of the orifice but will flow in complex patterns with eddies, swirls, and vortices. When the liquid leaves the orifice in this turbulent or, to use a more fashionable term, chaotic, state, the angular forces in the vortices will act against the surface tension of the liquid to strip off units of liquid to form droplets.

For a simple, classical analysis of the situation, assume that as the liquid leaves the orifice it has not only a linear velocity due to the pressure forcing it through the system but also some angular velocity ω resulting from its chaotic flow pattern. Liquid will therefore rotate within the jet with a period of $2\pi/\omega$. The rotation creates a local centrifugal force, F^{ω} . For a column of exiting liquid of radius r and height dz that force is given by

$$F_{\omega} = (2/3) \pi \rho r^3 \omega^2 dz \quad (11.8)$$

where ρ is the density of the liquid. The pressure disrupting the jet will be given by

$$P = (2/3) \rho \pi r^3 \omega^2 dz / 2 \pi r dz = (1/3) \rho r^2 \omega^2 \quad (11.9)$$

The surface tension forces keeping the jet together will be σ/r . The second radius of curvature for the jet in the direction of travel is being infinitely large. The critical radius at which a continuous jet of liquid becomes unstable and breaks up to form droplets will be

$$r_c = (3\sigma/r\omega^2)^{1/3} \quad (11.10)$$

It is difficult, of course, to determine the value of ω in a flowing system, so experimental verification of such an analysis is not a trivial matter. However, if one assumes that ω is proportional to the injection pressure, the product of the pressure and r^3 should be constant. In practice, the agreement is not quite exact. If one were to use an excess pressure – that is, the pressure in excess of that at which chaotic flow begins – the agreement might logically be expected to improve.

Since theories for predicting the drop size of a spray based on the characteristics of the liquid and the apparatus are complex and sometimes unsatisfactory, it is usually necessary to measure sizes for each given situation. In general, however, the following rules hold for most fluid ejection systems:

- 1) Increasing the surface tension of the liquid will increase the drop size.
- 2) Increasing the viscosity of the feed liquid will increase the drop size.
- 3) Increasing jet pressure decreases the average drop radius.
- 4) Increasing the nozzle diameter increases drop size.

The drop size for a given liquid system can also be controlled somewhat by the use of oval instead of round nozzle orifices, which will induce additional rotational force to the emerging liquid jet.

11.7.1.3 Rotary Atomization

In rotary atomization, a liquid is fed onto the center of a spinning disk or cup and accelerated to high velocity before being ejected into a gaseous atmosphere (Figure 11.7). Under ideal circumstances, the liquid is extended over the entire surface of the spinning element in a thin film. When it reaches the edge, the liquid can suffer one of three fates: (i) droplets may be formed directly at the edge (Figure 11.7a), (ii) the liquid may leave the surface in filaments that subsequently break up into droplets (Figure 11.7b), or the liquid may be detached as a sheet that later breaks up to form droplets (Figure 11.7c).

The operative mechanism of drop formation will be controlled by various system factors, including:

- 1) The viscosity and surface tension of the liquid.
- 2) The inertia or kinetic energy of the liquid at the edge.
- 3) Frictional effects between the liquid and the air it encounters at the edge.
- 4) Shear stresses present in the liquid as it leaves the spinning edge.

At relatively slow spin speeds and low liquid feed rates, viscosity and surface tension forces predominate. In that case, direct drop formation at the disk edge is usually found. The drops usually

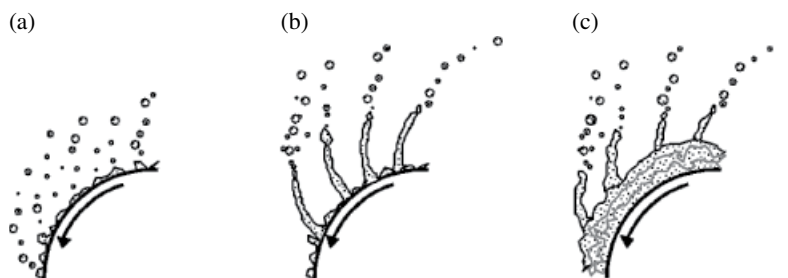


Figure 11.7 Mechanisms and location of drop formation in spinning disk or cup atomizers (a) direct edge drop formation at the disk edge, (b) drop formation from strings or filaments of liquid leaving the disk edge, and (c) drop formation from liquid sheets leaving the disk edge.

consist of a primary drop (relatively large) and several smaller “satellite” drops. Higher spin speeds and feed rates lead to drop formation from strings (mechanisms 2) and sheets (mechanism 3) in which inertial and frictional forces begin to dominate.

If the spinning disk is a smooth, flat surface, the spreading liquid will tend to “slip” over the surface and not attain the maximum theoretical tangential velocity expected based on the mechanical spinning speed. In effect, the liquid film loses traction on the disk surface and is not flung out toward the disk edge with maximum efficiency. The phenomenon is an example of wetting failure found in some linear high-speed coating operations and can lead to a significant amount of film defects. In most spraying operations the spinning disk is not smooth but has a series of vanes that “force” the liquid onto the surface, so more speed is attained before the liquid separates from the edge. That results in a smaller average drop diameter for the same spin speed. Cup-shaped elements are also employed in situations where very small particles are not required. The effect of changes in various conditions on the average particle size to be expected are given in Table 11.4.

The preceding brief treatment of aerosol drop formation by ejection processes illustrate that theoretical analysis can be used in predicting an approximate result based on a given set of circumstances. However, much more complex analyses are necessary to obtain more than a “ballpark” figure, and even then, the results may not justify the effort. In liquid aerosol formation, as in many such areas, experience is often the best guide.

11.7.2 Aerosol Formation by Condensation

A “chemical” method for the production of aerosol involves the direct condensation of drops or particles in the air or other gaseous environment. In order for a vapor to condense under conditions far from its critical point, certain conditions must be fulfilled. If the vapor contains no foreign substances that may act as nucleation sites for condensation, the formation of aerosol drops will be controlled by the degree of saturation of the vapor, analogous to the situation for homogeneous crystal formation.

The formation of a new phase by homogeneous nucleation involves first the formation of small clusters of molecules, which then may disperse or grow in size by accretion until some critical size is reached, at which point the cluster becomes recognizable as a liquid drop. The drop may then continue to grow by accretion or by coalescence with other drops to produce the final aerosol. Normally, extensive drop formation is not observed unless the vapor pressure of the incipient liquid is considerably higher than its saturation value, that is, unless the vapor is supersaturated.

Table 11.4 A summary of some basic rotary and nozzle atomizer and feed liquid characteristics and their expected effects on average drop size of the aerosol produced.

Characteristic	Expected effect of increase on drop size
Disk atomizer	
Disk diameter	Decrease
Disk speed	Decrease
Liquid feed rate	Increase
Liquid density	Increase
Liquid viscosity	Increase
Surface tension	Increase
Nozzle atomizer	
Orifice diameter	Increase
Liquid feed rate	Increase
Liquid feed pressure	Decrease
Liquid viscosity	Increase
Surface tension	Increase (small effect)

The barrier to the condensation of the liquid drop is related to the high surface energy possessed by a small drop relative to its total free energy. Thermodynamically, a simple argument can be given to illustrate the process. If one considers the condensation process as being

$$nA(\text{gas}, \mathbf{P}) \leftrightarrow A_n(\text{liquid drop})$$

where n denotes the number of molecules of gas A at pressure, \mathbf{P} , involved in the process; then in the absence of surface tension effects, the free energy change of the process will be given by

$$\Delta G = -nkT \ln \mathbf{P}/\mathbf{P}_0 \quad (11.11)$$

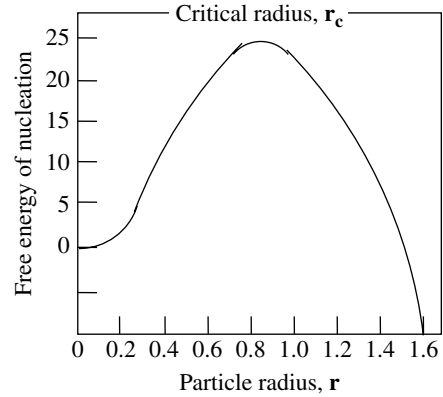
where \mathbf{P} is the pressure or activity of A in the vapor phase and \mathbf{P}_0 is that in the liquid phase. The ratio \mathbf{P}/\mathbf{P}_0 is often referred to as the degree of supersaturation of the system. A liquid drop of radius \mathbf{r} will have a surface energy equal to $4\pi\mathbf{r}^2\sigma$, so that the actual free energy change on drop formation will be

$$\Delta G = -nkT \ln \mathbf{P}/\mathbf{P}_0 + 4\pi\mathbf{r}^2\sigma \quad (11.12)$$

Both elements to the right in Eq. (11.12) can be written in terms of the drop radius, \mathbf{r} . If ρ is the density of the liquid and \mathbf{M} its molecular weight, the equation becomes

$$\Delta G = -\left(4/3\right)\pi\mathbf{r}^3\left(\rho/\mathbf{M}\right)RT \ln \mathbf{P}/\mathbf{P}_0 + 4\pi\mathbf{r}^2\sigma \quad (11.13)$$

Figure 11.8 In nucleation processes there will be a critical particle radius, r_c , below which free energy considerations will cause the incipient aerosol particle to evaporate. Above r_c , particle growth will occur.



where the two terms are of opposite sign and have a different dependence on r . A plot of ΔG vs. r exhibits a maximum as illustrated in Figure 11.8 for a hypothetical material with a density of 1, molar volume of 20, and pressure or activity ratio of 4 at a given temperature. The radius at which the plot is a maximum may be defined as the critical radius, r_c , which can be determined from Eq. (11.13) by setting $(\Delta G)/dr = 0$. That transformation gives the old faithful Kelvin equation, which on rearrangement leads to

$$r_c = 2\sigma V_m / RT \ln P/P_0 \quad (11.14)$$

where V_m is the molar volume of the liquid.

For water at 25 °C and supersaturation (P/P_0) of 6, Eq. (11.14) predicts a critical radius of 0.58 nm, corresponding to a cluster size of about 28 water molecules. It is difficult to say whether a drop of that small size actually has the same properties as the bulk liquid. It is probable, in fact, that the relatively high surface-to-volume ratio in such an assembly will result in an actual surface tension greater than the “true” bulk value of 72 mN/m. If a larger value for σ is used, the value of r_c decreases. The same occurs as the degree of supersaturation increases. The uncritical quantitative use of Eq. (11.14) can be misleading in that it predicts critical cluster sizes for homogeneous nucleation that are unlikely to occur with much frequency if left to the chance of random fluctuation processes. Qualitatively, however, the equation is useful in explaining the difficulty of forming liquid aerosols by direct condensation in highly purified systems.

If one combines Eqs. (11.13) and (11.14), it is possible to obtain a value for the free energy of formation of a cluster of the critical radius for drop formation, ΔG_{\max} :

$$\begin{aligned} \Delta G_{\max} &= 4\pi r_c^2 \sigma / 3 \\ &= 16\pi \sigma^3 V_m^2 / \left[3\rho^2 (RT \ln P/P_0^2) \right] \\ &= 16\pi \sigma V_m^{2/3} (RT \ln P/P_0)^2 \end{aligned} \quad (11.15)$$

Conceptually, one can think of the nucleation process in the following terms. If the pressure or activity of the vapor, P , is small relative to P_0 , then ΔG for a given cluster of molecules will increase with each added molecule. That is, the tendency will be for clusters smaller than r_c to return to the vapor phase.

Statistically, one might expect to encounter clusters of all sizes due to random fluctuation processes; however, all but the smallest would be very uncommon. There would therefore be little likelihood of obtaining the critical radius necessary for drop formation to occur. However, as the degree of supersaturation increases, r_c decreases, and random fluctuations begin to result in more clusters with that radius. Once that point is reached, the clusters begin to grow spontaneously to form drops. When a specific supersaturation pressure is exceeded, there will develop a steady parade of clusters of the required critical dimensions, resulting in the formation of a visible mist or fog.

11.7.3 Colloidal Properties of Aerosols

While aerosols are “typical” colloids in that they theoretically respond to the same forces as other members of the class – that is, electrostatic, dispersion, and van der Waals interactions – the special conditions that prevail in terms of the intervening gaseous medium result in a significant qualitative difference from colloids in liquid media. The importance of the intervening medium to the character and interactions of colloidal particles due to the screening effect of the continuous phase on the particle–particle interactions cannot be overemphasized. In aerosols, although the fundamental rules remain the same, the screening effect of the gaseous medium becomes relatively insignificant, so a number of adjustments in thinking must be made in order to reconcile the apparent differences between liquid and solid aerosols and foams, emulsions, and dispersions.

In a first analysis, we can identify at least four basic differences between aerosols and other colloids related to the dispersion medium: (i) buoyancy effects, (ii) the effects of movement of the dispersing medium, (iii) particle mobility in undisturbed conditions (i.e. free fall), and (iv) modification of interactions by the intervening medium. In emulsions, foams, and dispersions, buoyancy can be important in determining the stability of a system (i.e. matching the densities of dispersed and continuous phases can retard creaming or sedimentation). In aerosols, where the density of the continuous phase will always be significantly less than that of the dispersed particles, such effects are practically nonexistent – the colloid is essentially left to its own devices: the usual interactions found for all colloids, the “constant” pull of gravity (assuming we are not aboard the International Space Station), and the whims of the winds.

11.7.3.1 The Dynamics of Aerosol Movement

The study of the dynamics of fluid flow is concerned with the forces acting on the bodies in the fluid. In the basic analysis of foams, emulsions, and dispersions, fluid dynamics is largely ignored in favor of “true” colloidal interactions. In aerosols, the nature of the continuous medium makes the subject of fluid dynamics much more important to the understanding of the system, so the following discussion will introduce a few basic non-colloidal relationships that can be important in their study.

“Winds,” in the form of convection currents or other movements of the gaseous medium, are generally more important in gases than in liquids. Small temperature differences or mechanical movements that would be damped out quickly in a more viscous liquid may be translated over large distances in gases and produce a much greater effect in aerosols. (Remember the famous Chinese butterfly that can change the weather in Kansas according to chaos-based theories of weather development?)

In a static system of relatively high viscosity (relative to that of gases), inertial forces due to particle movement are not usually significant; that is, viscous forces dominate. In gases, the forces resulting from particle movement become more important and must be considered in a

dynamic analysis of the system. In dynamic fluid flow analysis, the ratio of inertial forces (related to particle mass, velocity, size, etc.) to viscous forces (a characteristic of the medium and not the particles) in a system is a dimensionless number termed the Reynolds number, R_e , and is used to define the type of flow occurring in the system – i.e. laminar or turbulent. For spherical particles of radius r and density ρ moving with a velocity v in a medium of viscosity η , the Reynolds number is given by

$$R_e = 2vR\rho/\eta \quad (11.16)$$

When $R_e < 1$ the system is said to be in laminar flow (Figure 11.9a) and the Stokes equation

$$D = kT/(6\pi\eta r) \quad (11.17)$$

is found to apply. In Eq. (11.17), D is the diffusion coefficient, η is the viscosity of the dispersion medium, r is the average particle radius, and k and T have their usual meanings. When $R_e > 10^3$ the system is said to be in fully turbulent flow (Figure 11.9b), and flow resistance is controlled by drag forces due to the medium, F_d , given by

$$F_d \cong 0.2\pi\rho_m R^2 v^2 \quad (11.18)$$

In the region $1 < R_e < 10^3$, a transition occurs from laminar ($F_d \propto v$) to turbulent flow ($F_d \propto v^2$), and the relationship between F_d and v becomes more complex. Also, since drag forces actually apply only to the relative velocity of the particle to the medium, the effects of drag or viscous resistance to flow for a dispersed particle must be adjusted to take into consideration the flow of the medium.

Even under ideal conditions, the dynamic flow behavior of aerosols vs. other colloids can be markedly different. In still air, the average distance a particle will travel before colliding with another particle, the mean free path, λ , is given by

$$\lambda = \left[(\sqrt{8})\pi\rho_N R^2 \right]^{-1} \quad (11.19)$$

where ρ_N is the particle number density. For an aerosol containing 10^8 particles/cm³ and radius 10^{-4} cm, $\lambda = 0.11$ cm. That is, a particle in random motion would travel an average of 0.11 cm before colliding with a neighboring particle. Such each collision may result in changes in the

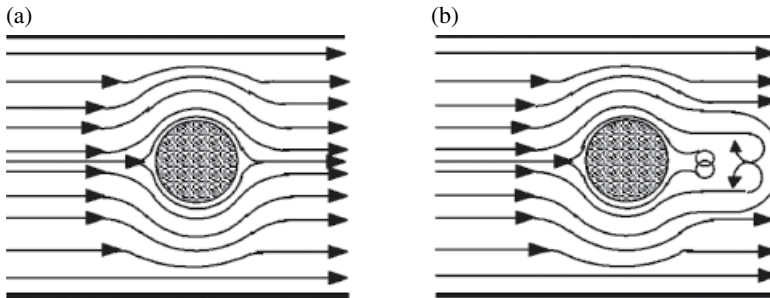


Figure 11.9 The movement of aerosol particles in the gas phase and its relation to the Reynolds number, R_e (a) $R_e < 1$ – laminar flow and (b) $R_e > 1000$ – turbulent flow.

characteristics of the system – momentum changes in the case of elastic collisions and possibly size changes for inelastic or “sticky” collisions.

According to the Stokes equation, the velocity of free fall of a particle in an undisturbed gravitational field, \mathbf{v}_f , is given by

$$\mathbf{v}_f = \mathbf{m}_a \mathbf{g} / 6\pi R \eta = 2R^2 g \rho / 9\eta \quad (11.20)$$

For simplicity, it is assumed that the density of the gas phase is small compared with that of the particle. For more accurate results, the density difference between particle and gas ($\rho = \rho_p - \rho_g$) should be employed. At 20 °C and atmospheric pressure, the viscosity of air is 1.83×10^{-4} cp (centipoises or g/cm/s), so for an aerosol drop of $R = 10^{-4}$ cm and $\rho = 0.92$ g/cm³ (a hydrocarbon, for example), the rate of fall will be approximately 0.011 cm/s. If the particle is emitted by an airplane flying at an altitude of 10000 m, the hypothetical drop will reach the ground after approximately 2.9 years! If the particle grows to a radius of 10^{-3} cm by coalescing with other drops, its rate of fall increases to 1.1 cm/s, and the same trip will take about 11 days. It is easy to understand why natural and unnatural events that produce high altitude aerosols can affect not only the color of our sunsets but also other more vital global atmospheric interactions.

11.7.3.2 Colloidal Interactions in Aerosols

Although the rules are the same, particle–particle interactions in aerosols appear to have significantly different characteristics than emulsions and dispersions in liquid media. A gaseous medium, because of its very different density, dielectric constant, and other properties, is very ineffective at screening the forces acting between colloidal particles. For that reason, aerosol particles, whether liquid or solid, will tend to have stronger attractive interactions among themselves and with other contacting surfaces than similar units in a liquid medium. The spontaneous formation of “fuzz balls” and dusty deposits (Figure 11.10) in the cleanest of homes is an all too common manifestation of the affinity of dispersed particles in aerosols. The illustration is, of course, for solid aerosols or dusts and smokes, but the concept is the same for liquid aerosol deposits, even though electrostatic effects may be reduced somewhat.

If we use as a measure of the kinetic energy of an aerosol particle the value of kT (Boltzmann’s constant \times absolute temperature), at ambient temperature that energy will be about 4×10^{-21} J. The colloidal forces in aerosols will be at least an order of magnitude greater, indicating that the attraction between particles will almost always overwhelm the kinetic energy of the particles and inelastic or sticky collisions will commonly occur.

Such attractive interactions can be particularly important in situations where the presence of even a few extraneous particles on a surface can be highly detrimental, as in the production of microchips for the electronics industry (Figure 11.11). The presence of a single dust particle on the

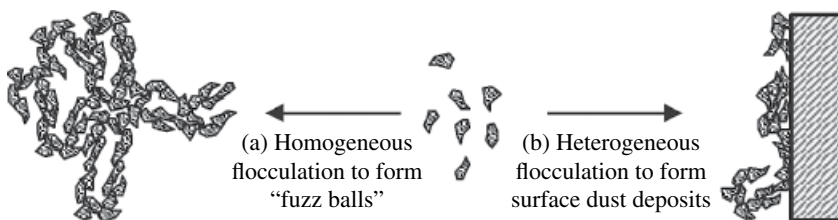


Figure 11.10 The aggregation of aerosol particles to form fuzz balls and dust layers due to the overwhelming attractive forces in gaseous media of low dielectric constant.

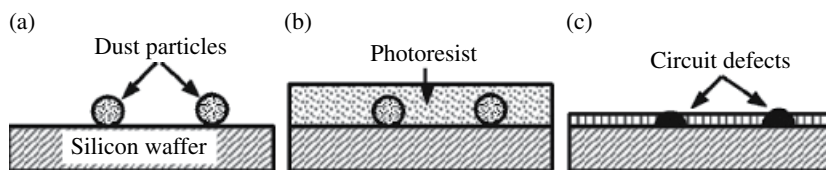


Figure 11.11 The importance of maintaining a clean, aerosol-free atmosphere is vitally important in the electronics industry (a) dust contaminated semiconductor surface, (b) photoresist coated over adhering dust particles, and (c) developed microcircuit with defects.

surface of a silicon wafer before coating with the photoresist resin that will be used to engrave the final circuit will, in all probability, result in a defective product in that area. When one considers that modern chips may have circuit line spacings of less than 10^{-4} cm, a particle of that diameter or even smaller will represent a veritable monkey wrench in the works. For that reason, extreme measures must be taken to ensure that aerosol particles are absent (to the extent technologically possible) in production areas.

In a “stable” cloud formation, the water drops lie in a size range in which air currents and other forces allow them to remain dispersed in a more or less stable way. Such clouds are usually the characteristic white because the small size of the light scattering particles produces less scattering of the incident sunlight. When droplets coalesce, as in rain formation in clouds, the identity of the small individual drops begins to be lost, and larger drops formed, producing the darker, heavier clouds characteristic of rain and thunder showers. The radius of the drop will greatly affect the free fall rate. If the drop forms under relatively calm conditions (e.g. little vertical convection to retard the drops’ fall), small, gentle rainfall will result. In cloud formations with high-velocity vertical convection currents (as in thunderstorms), the growing drops will be buoyed up by the air currents, allowing more time for drop growth and resulting in larger and more forceful rain. When the cloud formation reaches a high enough altitude and the drops are maintained suspended by strong internal convection currents, the drops may freeze to produce sleet or hail. The theory behind cloud seeding to produce rain is based on the introduction of charged colloidal particles, commonly silver iodide, that possesses a net electrostatic charge (usually positive) that will attract and coalesce small water particles (usually slightly negatively charged) producing drops heavy enough to fall as rain.

As a practical matter, almost all aerosol particles will rapidly acquire an electric charge leading to electrostatic interactions. The mechanisms for acquiring charge include direct ionization or ion exchange, specific ion adsorption, charge derived from specific crystal structures, and charge acquired as a result of contact or movement such as piezoelectric and impact charging. Because of the absence of a solvent, direct ionization will be of minor importance. Perhaps most important are charge acquisition due to friction (as in walking across a rug on a dry winter day and touching a doorknob), electron gain or loss due to collision with ionizing radiation, and adsorption of ions and charged dust particles from the air.

12

Solid Surfaces

Adsorption, Wetting, and Dispersions

The technological, environmental, and biological importance of adsorption from solution onto a solid surface can hardly be overestimated. The impact of such phenomena on our everyday lives is evident in such areas as foods and food science, agriculture, cosmetics, pharmaceuticals, mineral ore froth flotation, cleaning and detergency, the extraction of petroleum resources, lubrication, surface protection, and the use of paints and inks. Each of these applications, and many more, would be difficult if not impossible in the absence of the effects of adsorbed surfactants and stabilizers at the solid–liquid interface.

The presence of amphiphilic materials adsorbed at a colloidal interface may reduce interfacial energies to promote the formation of small particle sizes, enhance the wetting of the solid by a liquid phase, and provide a stabilizing surface layer to prevent or retard particle coagulation or flocculation. In addition, the action of surfactants in conjunction with dispersed drugs can greatly enhance the efficacy of drug delivery.

At the macroscopic level, the modification of a solid surface by adsorption can greatly affect its subsequent rewetting characteristics (waterproofing), its electrical properties (antistatic agents), its physical “feel” against human skin (fabric softeners), its interaction with contacting surfaces (lubrication), or its ability to adsorb other solutes (dyeing modifiers), just to name a few commonly encountered examples. Comprehensive discussions of some of the theoretical and practical aspects of surfactant adsorption at solid interfaces can be found in the references cited in Bibliography. In practically all of the above examples of surface modification by adsorption, and many more, the primary physical phenomena involved are pretty much the same. The following discussion introduces the basic concepts involved in terms of the natures of the adsorbing species and the surface being affected.

12.1 The Nature of Solid Surfaces

While the fluid interfaces discussed so far are relatively easy to treat from a thermodynamic standpoint because of the assumptions of molecular smoothness and homogeneity, assumptions that are not really accurate at the molecular level, solid surfaces present a number of formidable obstacles to the achievement of a clear, reasonably simple description of their surface energies and interactions with adjacent bulk phases and adsorbing species. As a result, many of the phenomenological aspects of adsorption at solid–liquid (S/L) and solid–vapor (S/V) interfaces are significantly more complicated and difficult to interpret than those at liquid–liquid (L/L) and liquid–vapor (L/V) interfaces. For the purpose of providing a clearer picture of the mechanics of surfactant

adsorption onto solids, then, it will be useful to briefly describe some of the special aspects of solid surfaces that differentiate them from fluid interfaces.

To better understand the properties of a solid surface, it is necessary to consider the possible structures of solids and their exposed surfaces. Solids and solid surfaces may be roughly divided into two main categories based on the nature of the arrangement of the constituent units. A solid may be crystalline, having reproducible intrinsic bulk properties such as a sharp melting point and a uniform pattern of packing of its constituent units (atoms, ions, or molecules) into a lattice structure, or it may be noncrystalline or amorphous, in which case the properties may be highly dependent on the previous history of the sample, and so tend to be variable and indefinite. A third class of solids is a heterogeneous mix of crystalline and amorphous structures scattered throughout the solid. Sodium chloride, for example, has a sharp melting point at 804 °C at atmospheric pressure, while a typical soda glass (sodium silicate) begins to soften at around 500 °C and becomes less rigid with increasing temperature. At 1500 °C the glass becomes completely molten and flows pretty much like any other liquid. There is no one temperature, however, that can be accurately identified as the true melting point, although one is generally defined in glass science based upon a somewhat arbitrarily chosen bulk viscosity value. Sodium chloride has a very well-defined crystal lattice structure, while the structure of glass is essentially random and without a defined repeat unit or unit cell. As examples of the third possibility, one can find certain polymers, such as polyethylene terephthalate or PET, which can be prepared in such a way as to have both crystalline and amorphous regions within the same bulk solid.

Another simple way of classifying solids for purposes of the present discussion is to define four types of solid structures based on the chemical nature of the structure. The four classifications used here include the following:

- 1) *Ionic solids* composed of a lattice structure of discrete ionic species. In an ionic solid (Figure 12.1a), the constituent units are ions, and each ion of a given charge is located approximately equidistant from a small number of ions of the opposite charge symmetrically arranged around it. The structure is thus held together primarily by the electrostatic attraction between

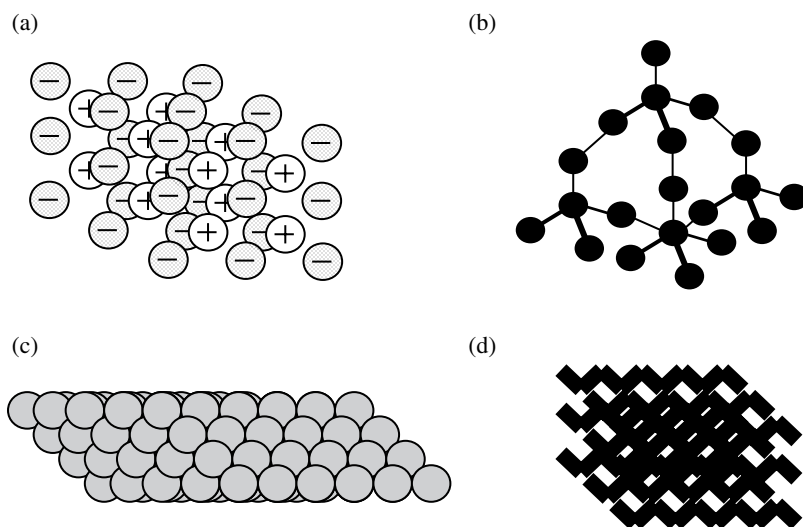


Figure 12.1 Schematic representations of the four main lattice types for crystalline materials (a) ionic crystal lattice, (b) homopolar diamond lattice, (c) metallic lattice, and (d) molecular lattice.

unlike charges, as reflected in the crystal lattice energy. Sodium chloride and most minerals fall into this general classification.

- 2) *Homopolar solids* in which the various units making up the solid are essentially identical, but do not involve ionic species. In a homopolar solid (Figure 12.1b), the basic units are neutral atoms bonded to a number of neighbors by covalent chemical bonds, as for example, in diamond, in which each carbon atom is bound to its four nearest neighbors to form a repeating tetrahedral unit, and graphite, in which carbon atoms are arranged in layered sheets of a hexagonally bonded flat structure.
- 3) *Metallic solids* in which the constituent units, the metal atoms, are repeated, but in which the presence of mobile electrons imparts special characteristics in terms of interfacial interactions. In a metallic lattice (Figure 12.1c), all of the atomic nuclei may be packed into a uniform pattern resembling a homopolar solid, but the valence electrons of each atom are hybridized into a range of energies allowing for the free movement of electrons throughout the crystal, thus producing the observed electrical conductivity of metals and other conductive materials.
- 4) *Molecular solids* in which the basic unit is a nonionic molecule that may present various surface characteristics depending on the atomic makeup and exact unit packing arrangement. A molecular solid (Figure 12.1d) is composed of an arrangement of molecules held together by attractive forces weaker in magnitude than the ionic and covalent forces active in the structures above. The “weaker” forces involved in molecular lattices, including van der Waals attractions, dipolar interactions, and hydrogen bonding or acid–base interactions, may also be present in the other lattice types but are generally of much less importance than the primary covalent and ionic forces. Because the interactions in molecular lattices are weaker, the distance of closest approach of adjacent molecules will be considerably greater than the bond distances between atoms within the molecule. Molecular solids may be either crystalline, amorphous, or a mixture of the two.

The distinctions among ionic, homopolar, and metallic structures are not, of course, absolute. A perfect ionic bond, for example, would require complete rigidity of the ionic species. In fact, the ions in such crystals behave more like deformed spheres, the degree of deformation, or polarization, following definite patterns. Anions, for instance, are generally more highly polarized than cations, and polarization susceptibility increases with the ionic radius. Because of the wide variability in the strength of ionic interactions in such materials, ionic solids exhibit a wide range of intensive and extensive properties, including surface energies.

Stearic acid crystals are a typical molecular solid within the current definition. In those materials, the shortest distance between carbon atoms in neighboring molecules is about 0.35 nm, compared with a covalent bond length of 0.154 nm. The packing density of molecules in such a lattice, then, would be expected to be lower than that found in the ionic, homopolar, or metallic cases. The surface energy of a material is directly related to the difference in the magnitude of the forces acting on an atom or molecule at the surface and that in the bulk. It is not surprising to find that ionic and metallic crystals, materials in which the magnitude of the lattice energies is high, possess high surface energies, ranging from several hundred to several thousand millijoules per square meter (mJ/m^2). Table 12.1 lists the surface energies of several types of solids. Because the lattice forces in most molecular solids are much lower than those in the other systems, such materials exhibit much lower surface energies.

The study of the surface chemistry of solids is concerned with specific properties of the atomic or molecular layers of material within a few molecular diameters of the interface with a vapor (or vacuum), a liquid, or another solid. To visualize the unique character of solid surfaces, it is helpful to compare the similarities and differences between solid and liquid surfaces.

Table 12.1 Experimentally determined surface energies of representative solids.

Surface	Surface energy (mJ/m ²)
Polyhexafluoropropylene	18
Polytetrafluoroethylene	19.5
Paraffin wax	25.5
Polyethylene	35.5
Polyethylene terephthalate	43
Quartz (SiO ₂)	325
Tin oxide (SnO ₂)	440
Platinum	1840

12.2 Liquid Versus Solid Surfaces

We know that the surface tension of a liquid is seen as arising from an imbalance of forces acting on molecules or atoms of the liquid at the surface relative to those in the bulk. A drop of liquid in equilibrium with its vapor, in the absence of any external forces, will assume a spherical shape that corresponds to a minimum surface-to-volume ratio. Work must be done on the drop to increase its surface area, implying that the surface molecules are in a higher energy state than those in the bulk. Such a state can be viewed as resulting from the fact that surface atoms or molecules have fewer nearest neighbors and, therefore, fewer intermolecular interactions. There is a free energy change associated with the reversible, isothermal formation of new liquid surface termed the “excess surface free energy.” The excess surface free energy is not the total energy of the surface, but the excess over that of the bulk material resulting from the units being located at the surface. The concept is illustrated in another way using a spring model in Figure 12.2.

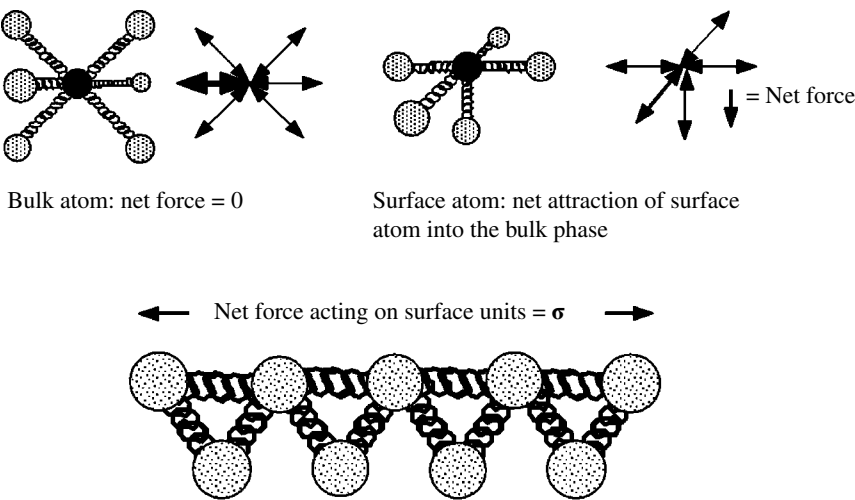
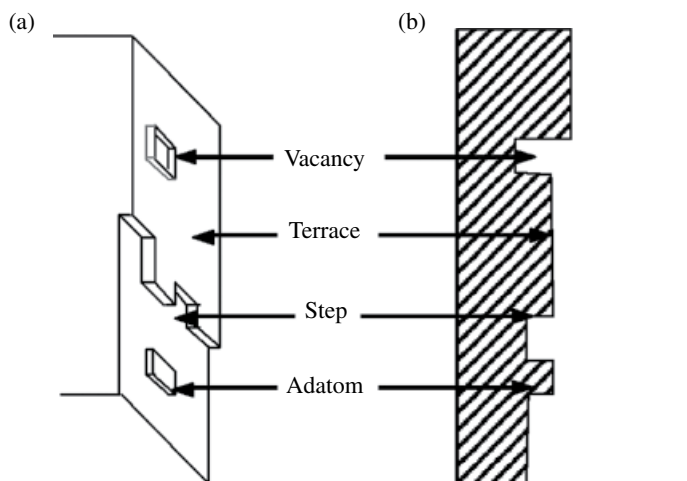


Figure 12.2 Schematic representation of a “spring” model of the origins of excess interfacial energies due to unbalanced, nonhomogeneous atomic (or molecular) forces acting upon atoms (molecules) in the interfacial region.

Figure 12.3 Typical solid surface defects that lead to nonuniform surface energies (a) angled surface view; (b) cross-sectional view.



Because of the thermodynamic imperative to attain a state of minimum free energy for the system as a whole, surface units are subjected to a net inward attraction normal to the surface. Geometrically, that can be equivalent to saying that the surface is in a state of net lateral tension defined as a force acting tangent to the surface at each point on it. It is this apparent tangential force that leads to the concept of a surface tension. The units of surface tension and of the excess surface free energy are dimensionally equivalent and, for pure liquids in equilibrium with their vapor, they are numerically equal when used to denote specific (i.e. per unit area) values.

In principle, all the concepts related to the surface energy of liquids can also be applied to that of solid surfaces. In practice, however, the situation is much more complex. When a fresh solid surface is formed by cleaving in a vacuum or its own vapor, the atoms, ions, or molecules in the new surface will not normally be able to immediately assume their equilibrium location or configuration because of the greatly reduced mobility in the solid state. Only mica is generally found to produce an approximately homogeneous, molecularly smooth surface under normal cleavage conditions. The surface of a solid, therefore, will usually have a nonequilibrium, nonuniform structure that may contain one or all of a number of defects, the presence of which will produce variations in energy across the surface. Some examples of such defects are shown in Figure 12.3. The surface energy of any given solid will therefore depend somewhat on its history and cannot be equated directly to the intensive thermodynamic properties of surface tension or specific excess surface free energy. Such variations in the surface energy of solids will also be reflected in the interaction of other phases with that surface, including the adsorption of surfactants. The problems of describing heterogeneous solid surfaces and related adsorption phenomena are most pronounced in inorganic surfaces, especially where electrostatic effects (charged species) may be present. As we shall see, the presence of charge sites on the solid surface will greatly affect (and often dominate) the adsorption of surfactants. In organic solids, surface heterogeneities are somewhat less important, although they cannot be ignored. As in the society of men, history can play an important role in the characteristics of all solid surfaces.

12.3 Adsorption at the Solid–Liquid Interface

Because of their inherently high surface energies, most newly formed solid surfaces, except those of very low energy polymers or waxes, will exhibit a strong tendency to adsorb almost any available material, including gases normally considered to be “inert” such as nitrogen, helium, argon, etc.

The adsorption of such materials has been extensively studied over the last century and has given rise to a broad quantitative understanding of the nature of solid surfaces and their adsorption characteristics. Such adsorption, however, differs significantly from that of surfactants and other amphiphiles, and the details are left for the adventurous reader to pursue.

The adsorption of surface-active materials onto a solid surface from solution is an important process in many situations including those in which we may want to remove unwanted materials from a system (detergency), change the wetting characteristics of a surface (waterproofing), control the triboelectric properties of a surface (static control), or stabilize a finely divided solid system in a liquid where stability may otherwise be absent (dispersion stabilization). In these and many other related applications of surfactants or amphiphilic materials, the ability of the surface-active molecule to situate itself at the solid–liquid interface and produce the desired effect is controlled by the chemical natures of the components of the system: the solid, the surfactant, and the solvent. The following discussions summarize some of the factors related to chemical structures that significantly affect the mechanisms of surfactant adsorption and the orientation with which adsorption occurs.

12.3.1 Adsorption Isotherms

The experimental evaluation of the adsorption from solution of amphiphilic materials at the solid–fluid interface usually involves the measurement of changes in the concentration of the adsorbed material in the contacting solution, for S/L interfaces, or the amount actually adsorbed onto the solid for S/V systems. The usual method for evaluating the adsorption mechanism is through the adsorption isotherm. The important factors to be considered are (i) the nature of the interaction between the adsorbate (the amphiphile) and the adsorbent (the solid); (ii) the rate of adsorption; (iii) the shape of the adsorption isotherm and the significance of plateaus in it; (iv) the extent of adsorption (i.e. monolayer or multilayer formation); (v) the interaction of solvent, if present, with the solid surface; (vi) the geometrical orientation of the adsorbed molecules at the interface; and (vii) the effect of environmental factors such as temperature, solvent composition, and pH on the adsorption process and equilibrium.

Early classifications of adsorption isotherms at solid–vapor interfaces were found to fit one of five basic shapes (Figure 12.4) at temperatures below the critical temperature (T_c) of the adsorbate. Type I isotherms were originally interpreted to represent monolayer adsorption of gas onto the solid surface, although it is subsequently realized that microporous adsorbents will produce similar isotherms. The remaining isotherms (II–V) represent various processes of multilayer adsorption.

Although most adsorption isotherms fall into two main categories, many subtle and not-so-subtle shape variations have been reported, leading to a more complex classification system as illustrated in Figure 12.5. That classification system gives four basic isotherm shapes based on the form of the isotherm at low concentrations; the subgroups are then determined by their behavior at higher concentrations.

The Langmuir (L class) isotherm is the most commonly found and is characterized by having its initial region (L1) concave to the concentration or horizontal axis. As the concentration of adsorbate increases, the isotherm may reach a plateau (L2), followed by a section convex to the concentration axis (L3). If the L3 region attains a second plateau, the region is designated L4. Under some circumstances, such as surfactants and some dyes that aggregate in solution and contain highly surface-active contaminants, a maximum may be obtained (L5; not shown in Figure 12.5). Since it is thermodynamically impossible for a pure system to exhibit such a maximum, its existence can represent a telltale sign of the presence of impurities.

Figure 12.4 Basic adsorption isotherm shapes for vapors on solids below T_c of the adsorbate.

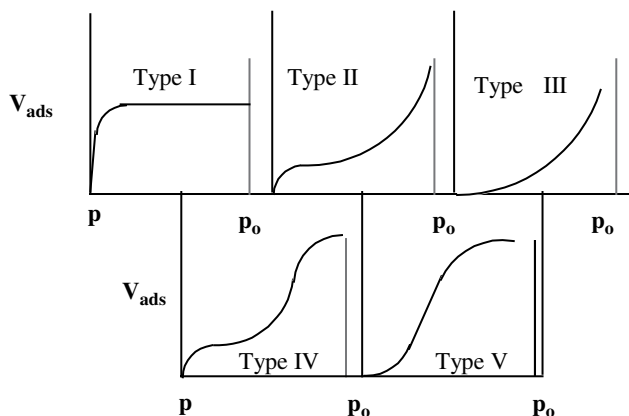
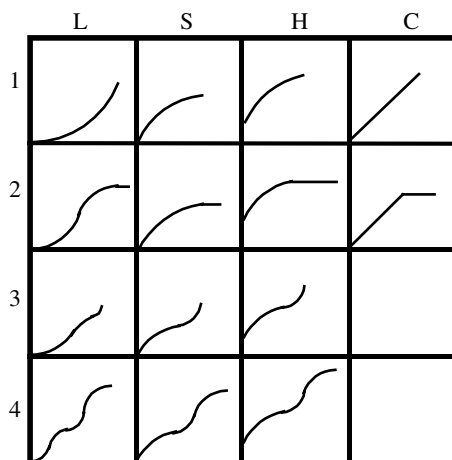


Figure 12.5 Modes of surfactant adsorption through nonpolar dispersion forces.



In the S class of isotherms, the initial slope is convex to the concentration axis (S1) and is often broken by a point of inflection (S2) leading to the characteristic S shape (S3). Further concentration increases may then parallel those of the L class, including the presence of a maximum. The high affinity or H class of adsorption isotherm occurs as a result of very strong adsorption at low adsorbate concentrations. The result is that the isotherm appears to have a positive intercept on the ordinate. Higher concentrations lead to similar changes to those found in the L and S classes.

The final type of isotherm is the C class. Such systems exhibit an initial linear portion of the isotherm indicating a constant partitioning of the adsorbate between the solution and the solid. Such isotherms are not found for homogeneous solid surfaces but are found in systems in which the solid is microporous. The classification system illustrated in Figure 12.5 has proven very useful in providing information about the mechanism of adsorption in many systems. An excellent discussion of many of the details is given in the reference to Parfitt and Rochester given in Bibliography.

12.3.2 Mechanisms of Surfactant Adsorption

The adsorption of surface-active agents at the interface of a solid and a liquid phase is a fundamentally important phenomenon, both scientifically and technologically. The facility and strength of

that adsorption are very largely controlled by three factors, which are related to the materials in question, namely, (i) the chemical nature of the species being adsorbed, including the nature of the head group (anionic, cationic, nonionic, etc.) and that of the hydrophobe (length and nature of the chain, degree of branching, etc.); (ii) the nature of the solid surface onto which the surfactant is being adsorbed (highly charged, nonpolar, etc.); and (iii) the nature of the liquid environment (in water, the pH, electrolyte content, temperature, additives, etc.). A slight change in one of these or other factors can result in a significant change in the adsorption characteristics of the system.

The adsorption of a surfactant molecule onto a solid surface can be significantly affected by relatively small changes in the characteristics of the system. Such sensitivity results from the wide range and strengths of adsorption mechanisms that may be operative. Except in some cases of surfactant–polymer interaction discussed in Chapter 9, it is usually found that adsorption occurs on a molecular level. The mechanisms of adsorption available generally parallel those operative in all intermolecular interactions – electrostatic and dipolar attractions, van der Waals forces, etc. The strengths of such interactions range from the relatively weak but long-distance dispersion forces resulting from the nature of electron motion in molecular (and atomic) orbitals to the stronger, more specific, but shorter-range interactions between surfactants and solid surfaces of opposite electrical charge.

12.3.2.1 Dispersion Forces

Since dispersion force interactions are essentially statistical mechanical, they have been extensively analyzed from a theoretical standpoint and are reasonably well understood, conceptually at least. Although relatively weak (≈ 8 kJ/mol), they are generally considered to be long-range forces, since their influence can sometimes be detected over several hundreds of nanometers. The effect of hydrocarbon chain length within a homologous series of ionic surfactants observed on adsorption onto a given solid surface is generally considered to indicate that such systems follow Traube's rule; that is, many of the characteristics of a material, including surface tension and adsorption, will vary regularly with the molecular weight of the species, other things being equal.

The adherence of surfactants to Traube's rule has been the subject of many investigations. It has generally been found that adsorption increases with an increase in the molecular weight of the hydrophobic portion of the surfactant molecule. The longer the hydrocarbon chain in a given series, the larger the amount of surfactant adsorbed at saturation, and the lower the total surfactant concentration at which saturation occurs. As seen in Chapter 6, the critical micelle concentrations of the same series will decline in a similar way. Since saturation adsorption often occurs coincident with the initiation of micelle formation, it is inferred that the two phenomena are related. Some authors have pointed out that if adsorption isotherms for a homologous series of surfactants are plotted as a function of the concentration at saturation, C_a , divided by the **cmc**, the results will be almost superimposable. Such a relationship is not always clear-cut, however, since some systems show a maximum in adsorption, with the total amount of adsorbed material decreasing as the **cmc** is exceeded. Such systems usually reflect the presence of a surface-active impurity or a mixture of homologues in which the more surface-active component is adsorbed initially but is desorbed and solubilized in micelles once present.

Regardless of the specifics of the adsorption mechanism due to dispersion forces, the result is important scientifically and technologically because it is always present, whether as an independent effect or acting in conjunction with the other mechanisms discussed below. The importance of the effect in conjunction with other forces is illustrated by the propensity for surfactants with longer hydrophobic tails to displace similarly charged lower molecular weight materials and inorganic ions from solid surfaces.

Dispersion forces are usually discussed in terms of being attractive and commonly are so for identical or similar materials, although many situations arise in which they may actually have a net repulsive effect, especially in three-component systems. The theoretical aspects of such repulsive dispersion interactions are not covered here. However, in relation to the situation of attractive dispersion forces between surfactant molecules and a solid surface leading to adsorption, hydrophobic bonding may be considered to be “pushing” in character, in that it might be interpreted conceptually as pushing the surfactant molecule out of the aqueous environment onto the adsorbent surface or into micelles. As mentioned previously and discussed in more depth in Chapter 6, one of the main driving forces for the formation of micelles in aqueous solution, and the adsorption of surfactants at interfaces, is the tendency of hydrophobic groups to want to “escape” from the aqueous environment (or for the aqueous environment to push the hydrophobic groups out). The thermodynamically unfavorable situation of the structured water molecules necessary for the solvation of the hydrophobic tail of the surfactant and the mutual attraction of the tails due to dispersion attractions leads to micelle formation. Similarly, in the presence of a solid surface, the adsorption of surfactant molecules may be enhanced by the “push” to remove themselves from the water structure. The aggregation of surfactant molecules on the solid surface would then be a manifestation of both these mechanisms (Figure 12.6).

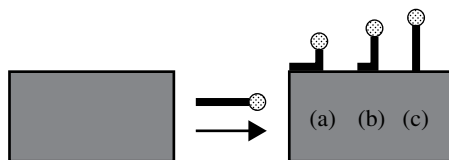


Figure 12.6 Modes of surfactant adsorption through nonpolar dispersion forces: (a) trains, (b) “Ls,” (c) perpendicular (or almost so).

12.3.2.2 Polarization and Dipolar Interactions

Somewhere between the strictly nonpolar dispersion and hydrophobic adsorption mechanisms and the dipolar and electrostatic effects discussed below lie the molecular interactions resulting from induced dipolar or polarization effects. When one component of an adsorbing systems – usually, but not always, the surfactant – contains an electron-rich group (an aromatic nucleus, for example) and the other a strongly polarizing site such as a positive charge, there exists the possibility for the induction of a dipole in one species leading to a significant improvement in the ease of adsorption. The strength of such interactions usually lies in the range of 4–8 kJ/mol, in the same range as dispersion force interactions. Such induced polarization usually is encountered in conjunction with adsorption resulting from other forces as well.

Less well defined than most atomic and molecular interactions, but potentially more important as a mechanism of adsorption in aqueous systems, is that resulting from acid–base interactions and hydrogen bond formation between the adsorbent and water or surfactant (Figure 12.7). The presence (or absence) of such interactions can greatly alter the extent and mode of surfactant adsorption and therefore greatly alter the macroscopic effects of the process.

An interesting example of the potential importance of such interactions can be seen in the example of a pure, clean quartz surface. If the surface has been heated to a sufficiently high temperature (>200 °C), a drop of distilled water placed on the surface will form a sessile drop with a nonzero contact angle, usually in the range of 30°. The heat treatment of the quartz produces a dehydrated surface composed of Si–O–Si bonds that, while

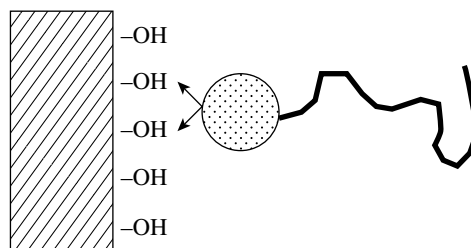


Figure 12.7 Adsorption via polar, hydrogen bonding, or acid–base interactions.

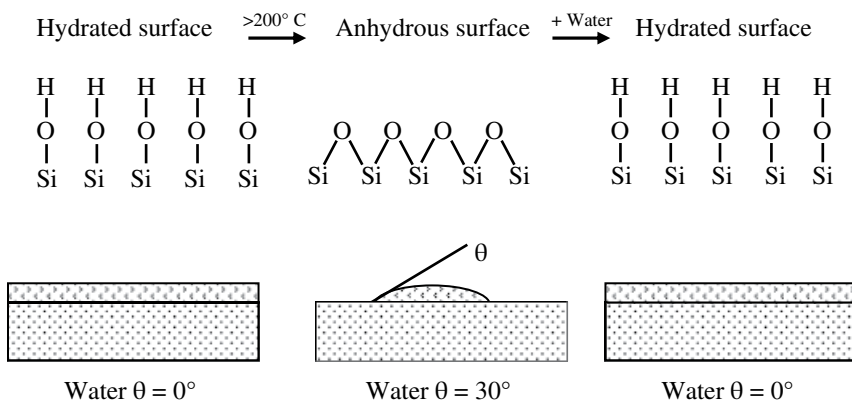


Figure 12.8 Effects of changes in the nature of a solid surface on interactions involving hydrogen bonding or acid–base chemistry, as illustrated for the contact angle (θ) of water on a silica surface.

polar, are not strongly interacting in terms of hydrogen bonding. If the same surface is allowed to hydrate so that the surface layer is now basically composed of $-\text{SiOH}$ groups, a drop of water will spread completely on the surface. The effect is illustrated schematically in Figure 12.8.

12.3.2.3 Electrostatic Interactions

At the end of the spectrum of adsorption mechanisms opposite to the universal dispersion forces lie those interactions resulting from the presence of discrete electrical charges on the surfactant molecules and the solid adsorbent. Those interactions may be described as being either ion pairing or ion exchange (Figure 12.9). The distinction between the two mechanisms lies in the fact that in

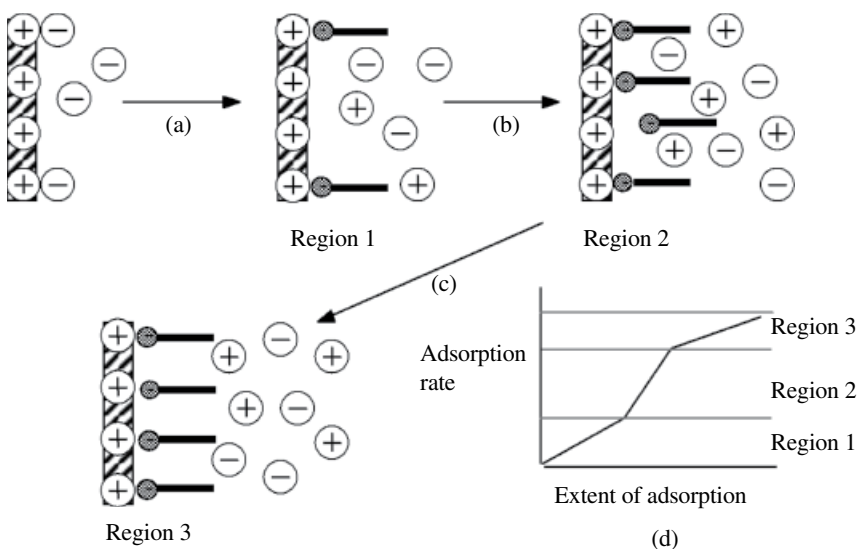


Figure 12.9 Proposed mechanisms to explain various rates of ionic surfactant adsorption as a function of surface coverage and mode of adsorption (a) native surface, (b) ion exchange, (c) ion pairing, (d) charge neutralization, and (e) representative isotherm.

ion exchange, the adsorbing surfactant molecule displaces a similarly charged counterion adsorbed on the substrate surface, while in ion pairing, the surfactant adsorbs onto an oppositely charged site, which was not previously occupied by a counterion. This distinction may seem rather fine at first glance, but it can be significant in determining and understanding the resultant effects of such adsorption.

When one considers adsorption as a result of dispersion, hydrophobic, and, to some extent, polarization mechanisms, it is generally assumed that the solid substrate presents a homogeneous surface on which adsorption is essentially random. As seen above, the assumption of homogeneity for solid surfaces is not necessarily valid, although it may be difficult to isolate the individual effects of surface defects. In the event that discrete electronic charges are present, the situation is further complicated by the presence of an electrical double layer, which can significantly alter the adsorption process.

12.3.3 The Electrical Double Layer

The existence of electrical charges at any interface will give rise to electrical effects, which will, in many cases, determine the major characteristics of that interface. Those characteristics will affect many of the properties of a multicomponent system, including emulsion and foam formation and stability, solid dispersions, and aerosols. The theoretical and practical aspects of electrical double layers are the subject of a vast amount of literature and for that reason have not been addressed in any detail so far. Such details can be found in bibliographic references cited for this chapter.

Any interface that has an unbalanced electrical charge distribution will result in the formation of a net electrical charge of one sign on one side of the interface and a charge of opposite sign on the other side. Such a situation gives rise to what is called the electrical double layer. Since electrical neutrality must be conserved, the net charge on both sides of the interface will be zero. However, differences in the mobility of the different charges may give rise to wide differences in the distribution of the charges, especially those in a liquid phase associated with a charged solid surface (Figure 12.10).

A major field of investigation in modern colloid and interface science has been the search for a means to predict and determine the exact distribution of electrical charges at or near a solid–solution interface. Building on the original theories of Helmholtz, a model has developed that allows for a reasonable description of how the electrical potential behaves in relation to the distance from the solid charged surface. The model includes the disposition of counterions tightly bound to the surface (the Stern layer) and those more weakly held in the diffuse portion of the double-layer region.

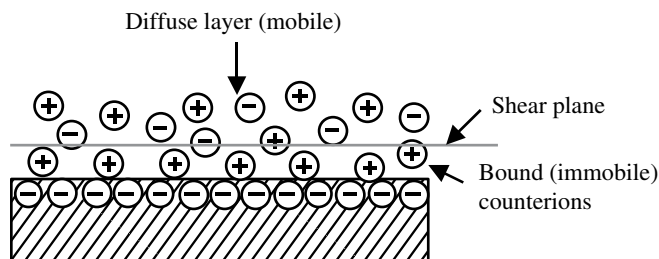


Figure 12.10 A schematic representation of the origin of the diffuse electrical double layer.

The effective thickness of the diffuse layer can be calculated to determine the distance from the surface at which the electrical properties of the layer are essentially those of the bulk solution. Often termed the Debye length, κ , the effective thickness is given by

$$1/\kappa = \left[(\epsilon_r \epsilon_0 R T) / (4\pi F^2 \sum C_i Z_i^2) \right]^{1/2} \quad (12.1)$$

where $\epsilon_r = \epsilon/\epsilon_0$ is the relative static dielectric constant of the solution (ϵ is the static permittivity of the solution and ϵ_0 is that of a vacuum), F the Faraday constant, and C_i the molar concentration of the i th ion of valence Z in the solution and R and T have their usual meanings.

From Eq. (12.1) it is seen that $1/\kappa$ is inversely proportional to the valence of the counterions, Z , and the square root of C_i . It is proportional to the square roots of T and ϵ . It is to be expected, therefore, that in solvents of high dielectric constant such as water, electrical effects will be felt much further into the solution. In low dielectric constant media such as hydrocarbons, electrical effects are very short ranged and usually have little practical significance. Of great practical importance in all situations are the value of Z and C_i . For 1 : 1 ($M^+ X^-$) electrolytes in 0.01 M solution at room temperature, the value of $1/\kappa$ is approximately 3.0 nm; as the electrolyte concentration is raised to 0.1 and 1.0 M, the values decrease to approximately 1.0 and 0.3 nm, respectively. More significantly, as the value of Z is changed from 1 to 2 and 3, with all other factors, including C_i , being held constant, the value of $1/\kappa$ falls very rapidly, and the effectiveness of the electrical forces at influencing the system is rapidly lost.

The potential importance of the double layer to adsorption in charged systems can be seen from the fact that the relationship in Eq. (12.1) predicts that potential interactions between surface charges and ions in solution will be significantly affected by the conditions in the solution phase. Double-layer theory is most important in the general field of colloidal stability, in which the concentration and valence of ions present can dramatically affect the stability and utility of an electrostatically stabilized colloidal system.

12.4 The Mechanics of Surfactant Adsorption

When the adsorption of a surfactant onto a solid surface is considered, several quantitative and qualitative points are of interest, including (i) the amount of surfactant adsorbed per unit mass or area of solid, (ii) the solution surfactant concentration required to produce a given surface coverage or degree of adsorption, (iii) the surfactant concentration at which surface saturation occurs, (iv) the orientation of the adsorbed molecules relative to the surface and solution, and (v) the effect of adsorption on the properties of the solid relative to the rest of the system. In all cases, it is assumed that such factors as temperature and pressure are held constant.

The classical method for determining the degree of adsorption in a given system is by way of the adsorption isotherm. The basic equation describing the adsorption of one component of a binary solution onto a solid substrate is given as

$$n_0 \Delta x / m = n_1^s x_2 - n_2^s x_1 \quad (12.2)$$

where n_0 is the total number of moles of solution before adsorption, Δx is the change in mole fraction of component 2 with respect to 1 after adsorption, m is the mass of solid in contact with the solution, n_1^s and n_2^s are the number of moles of components 1 and 2 adsorbed onto the surface per gram of solid at equilibrium, and x_1 and x_2 are the mole fractions of components 1 and 2, respectively, in the liquid phase.

In the case of a dilute surfactant solution where the surfactant (component 2) is much more strongly adsorbed than the solvent (component 1), the equation simplifies to

$$n_2^s = \Delta n_2 / m = (C_2^\circ - C_2) V / m = \Delta C_2 V / m \quad (12.3)$$

where C_2° is the molar concentration of component 2 before adsorption, C_2 is its molar concentration at adsorption equilibrium, $\Delta C_2 = C_2^\circ - C_2$, and V is the volume of the liquid phase in liters.

For surfactant systems, the concentration of adsorbed material can be calculated from the known amount of material present before adsorption and that present in solution after adsorption equilibrium has been reached. A wide variety of analytical methods for determining the solution concentration of surfactants are available, and almost all have been used at one time or other. The utility of a specific method will depend ultimately on the exact nature of the system involved and the resources available to the investigator.

12.4.1 Adsorption and the Nature of the Adsorbent Surface

As indicated above, the nature of the solid surface involved in the adsorption process is a major factor affecting the manner and extent of surfactant adsorption. At this point it might be useful to briefly discuss some of the specific effects of solid surface characteristics on the mode of adsorption, as well as to clarify the meaning of “efficiency” and “effectiveness” as applied in the context of surfactant adsorption.

In the current context, “efficiency” is intended to define the equilibrium concentration of surfactant, C_o , in the liquid phase required to produce a given level of adsorption under defined conditions of temperature, pressure, solution composition, etc. The “effectiveness” of adsorption refers to the amount (concentration) of surfactant actually adsorbed on the solid surface at surface saturation. The effectiveness of adsorption of a given surfactant can, of course, be determined directly from the adsorption isotherm.

When one considers the possible nature of an adsorbent surface, three principal groups readily come to mind: (i) surfaces that are essentially nonpolar and hydrophobic, such as polyethylene, polypropylene, Teflon, etc., (ii) those that are polar but do not possess discrete surface charges such as polyesters and natural fibers such as cotton, and (iii) those that possess strongly charged surface sites. Each of these surface types is discussed, beginning with what is probably the simplest, the nonpolar, hydrophobic surface.

12.4.2 Nonpolar, Hydrophobic Surfaces

Adsorption of surfactants onto nonpolar surfaces is by dispersion force interactions. From aqueous solution, it is obvious that the orientation of the adsorbed molecules may be such that the hydrophobic groups are associated with the solid surface with the hydrophilic group directed toward the aqueous phase. In the early stages of adsorption, it is likely that the hydrophobe will be lying (approximately) on the surface much like trains or L's (Figure 12.11a, b). As the degree of adsorption increases, however, the molecules will gradually be oriented more perpendicular to the surface until, at saturation, an approximately close-packed assembly results (Figure 12.11c).

It is generally found that surface saturation is attained at or near the **cmc** for the surfactant. In many cases the isotherm is continuous, while in others an inflection point may be found. The existence of the inflection point is usually attributed to a relatively sudden change in surfactant orientation – from train or L-shaped to a more perpendicular arrangement.

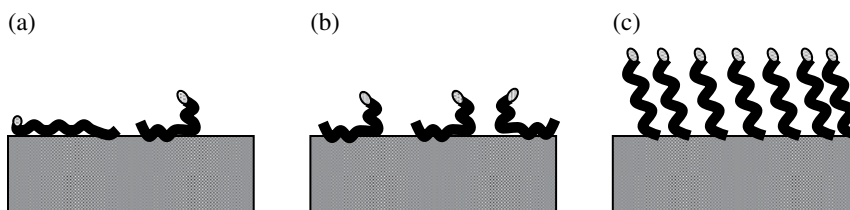


Figure 12.11 Adsorbed surfactant orientation as a function of surface coverage on a nonpolar surface (a) low coverage, primarily trains; (b) intermediate coverage, trains and “Ls”; and (c) surface saturation, approximately vertical, close-packed, with near minimum area per molecule, although some tilt may be present.

The adsorption of surface active agents onto nonpolar surfaces from nonaqueous solvents has been much less intensively studied than aqueous systems. Generally, work has been limited to various carbon black dispersions in hydrocarbon solvents. The orientation of the adsorbed molecules in such systems appears to remain more or less parallel to the surface, although the exact details are found to depend greatly on the history of the carbon surface.

An important consequence of adsorption of surfactants onto a nonpolar surface is that the net character of the surface is drastically changed. If the adsorbed species is charged, the adsorbed layer imparts, to some extent at least, the characteristics of such a surface, with all of the attending strengths (e.g. increased stability in dispersed systems) and weaknesses (sensitivity to electrolyte). If the adsorbed material is nonionic, the same will generally hold true. More on surface modification by adsorbed species is given later.

12.4.3 Polar, Uncharged Surfaces

Polar, uncharged surfaces include many of the synthetic polymeric materials such as polyesters, polyamides, and polyacrylates, as well as many natural materials such as cotton. As a result, the mechanism and extent of surfactant adsorption onto such materials has great potential technological importance. The mechanism of adsorption onto these surfaces will be more complex than that of the nonpolar case discussed above, since such factors as orientation will be determined by a balance of several forces.

The potential forces operating at a polar surface include the ever-present dispersion forces, dipolar interactions, and hydrogen bonding and other acid–base interactions. The relative balance between the dispersion forces and the uniquely polar interactions is of importance in determining the mode of surfactant adsorption. If the dispersion forces predominate, for example, adsorption will occur in a manner essentially equivalent to that for the nonpolar surfaces (Figure 12.11). If, on the other hand, polar interactions dominate, adsorption may occur in a reverse mode; that is, the surfactant molecules will be more oriented with the hydrophilic head group toward the solid surface and, by necessity, the hydrophobic group set more toward the aqueous phase (Figure 12.6b) or held more or less parallel to the solid surface. Orientation of the hydrophobic tail toward the aqueous phase can introduce its own complications and can lead to some sort of hemi-micelle aggregation on the surface, at least until monolayer saturation is reached, after which a bilayer can begin to form. For now, such surface aggregation is somewhat speculative. Obviously, the net results of the two adsorption modes will be drastically different. Such differences may be of particular importance in the areas of adhesion and lubrication, where the orientation of adsorbed species could significantly affect the performance of the system.

12.4.4 Surfaces Having Discrete Electrical Charges

The final class of adsorbent surface is the most complex of the three for several reasons. From the standpoint of the nature of the surface, these materials are capable of undergoing adsorption by all the previously mentioned mechanisms. Possibly more important, however, is the fact that adsorption involving charge–charge interactions is significantly more sensitive to external conditions such as pH, the electrolyte content of the aqueous phase, and the presence of non-surface-active co-solutes than are the other mechanisms.

Materials possessing charged surfaces include almost all the inorganic oxides and salts of technological importance (silica, alumina, titanium oxide, etc.), silver halides, latex polymers containing ionic co-monomers, many natural surfaces such as proteins, and cellulose. It is very important, therefore, to be able to understand the interactions of such surfaces with surfactants in order to optimize their effects in such applications as paint and pigment dispersions, paper making, textiles, and pharmaceuticals.

Because of the large number of possible interactions in systems containing charged surfaces and ionic surfactants, it is very important to closely control all the variables in the system. As adsorption proceeds, the dominant mechanism may go from ion exchange through ion binding to dispersion or hydrophobic interactions. As a result, adsorption isotherms may be much more complex than those for the simpler systems.

The adsorption isotherms for surfactants on surfaces of opposite charge generally show three well-defined regions of adsorption in which the rates vary because of changes in the mechanism of adsorption. One interpretation of such adsorption involves three consecutive mechanisms (Figure 12.9b–d). In the early stages (region 1), adsorption occurs primarily as a result of ion exchange in which closely associated “native” counterions are displaced by surfactant molecules. During that stage the electrical characteristics (i.e. the surface charge or surface potential) of the surface may remain essentially unchanged. As adsorption continues, ion pairing of surfactant molecules with surface charges may become important (region 2), resulting in a net decrease in surface charge. Such electrical properties as the zeta potential, a measure of the surface charge density (C/m^2), will tend toward zero. It is often found that in region 2 the rate of adsorption will increase significantly. The observed increase may be due to the cooperative effects of electrostatic attraction and lateral interaction among adjacent hydrophobic groups of adsorbed surfactants as the packing density increases.

As the adsorption process approaches the level of complete neutralization of the native surface charge by adsorbed surfactant, the system will go through its zero point of charge (zpc), where all the surface charges have been paired with adsorbed surfactant molecules. In that region (region 3), hydrophobic interactions between adjacent surfactant tails can predominate, often leading to the formation of aggregate structures or hemi-micelles already postulated. If the hydrophobic interaction between surfactant tails is weak (because of short or bulky structures) or if electrostatic repulsion between head groups cannot be overcome (because of the presence of more than one charge of the same sign or low ionic strength), the enhanced adsorption rate of region 2 may not occur, and hemi-micelle formation may be absent. An additional result of the onset of dispersion force-dominated adsorption may be the occurrence of charge reversal as adsorption proceeds. That aspect is covered in more detail later.

Surfaces possessing significant surface charge in aqueous solvents are especially sensitive to environmental conditions such as electrolyte content and the pH of the aqueous phase. In the presence of high electrolyte concentrations, the surface of the solid may possess such a high number of bound counterions that ion exchange is the only mechanism of adsorption available other than dispersion or hydrophobic interactions. Not only will the electrical double layer of the surface be

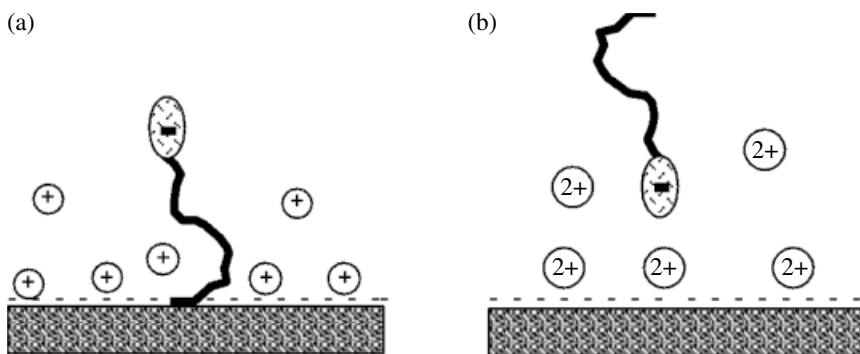


Figure 12.12 The role of polyvalent ions as potential bridging ions for the adsorption of anionic surfactants on negatively charged surfaces (a) normal adsorption of a surfactant on a surface of the same electrical charge and (b) cation bridging leading to “inverted” adsorption.

collapsed to a few nanometers thickness, but attraction between unlike charge groups on the surface and the surfactant and repulsion between the like charges of the surfactant molecules will be suppressed. The result will often be an almost linear adsorption isotherm, lacking any changes in slope characteristic of the mechanism changes described above.

While an increase in the electrolyte content may cause a decrease in adsorption of surfactants onto oppositely charged surfaces, it may allow an increase in adsorption of like charged molecules. That trend holds true for both the efficiency and the effectiveness of adsorption. The presence in the solution of polyvalent cations such as Ca^{2+} or Al^{3+} will generally increase the adsorption of anionic surfactants. Such ions are characteristically tightly bound to a negatively charged surface, effectively neutralizing charge repulsions. They also can serve as an efficient bridging ion by association with both the negative surface and the anionic surfactant head group (Figure 12.12).

Adsorption onto solid surfaces having weak acid or basic groups such as proteins, cellulose, and many polyacrylates can be especially sensitive to variations in solution pH. As the pH of the aqueous phase is reduced, the net charge on the solid surface will tend to become more positive. That is not to say that actual positive charges will necessarily develop; rather, ionization of the carboxylic acid groups will be suppressed. The net result will be that the surface may become relatively more favorable for the adsorption of surfactants of like charge (e.g. anionic surfactants onto carboxyl surfaces) and less favorable for adsorption of oppositely charged surfactants. For surfaces containing weak basic groups such as amines, the opposite would be true. That is, lowering the pH will lead to ionization of surface basic groups, increased adsorption of oppositely charged (anionic) molecules, and decreased interaction with materials of the same charge.

An increase in the temperature of an adsorbing system will usually result in a decrease in the adsorption of ionic surfactants, although the changes will be small when compared with those due to pH and electrolyte changes. Nonionic surfactants, which usually have an inverse temperature/solubility relationship in aqueous solution, will generally exhibit the opposite effect. That is, adsorption will increase as the temperature increases, often having a maximum near the cloud point of the particular surfactant.

The discussion of some of the primary effects of the solid surface character on the adsorption of surfactants admittedly has been brief and lacking in experimental detail. However, a number of excellent books and reviews cover the subject from a theoretical and experimental viewpoint in great depth.

12.5 Surfactant Structure and Adsorption from Solution

In this section, we turn our attention to surfactant adsorption phenomena from the viewpoint of the surfactant chemical structure, and we discuss more of the effects of external environmental factors. As usual, there is no intention to provide a complete literature review of the state of our knowledge related to surfactant structure and adsorption behavior. Rather, the discussion summarizes what is generally understood about the complex relationships among surfactant structure, solid surface characteristics, and solution environmental factors, leaving the search for more theoretical details to the interested reader. For the sake of consistency, the discussion is divided according to the surface types, as was done in the preceding section, although the order of discussion has been reversed.

12.5.1 Surfaces Possessing Strong Charge Sites

As we have seen, the primary surfactant characteristic controlling the “sense” of surfactant adsorption (i.e. the head directed outward into the liquid phase or toward the surface) onto surfaces with strong charges is the nature of the hydrophilic group of the surfactant. Obviously, for surfactants with charge opposite to that of the surface, electrostatic attraction would be expected to dominate in aqueous solution, while for systems of like charge, any adsorption would be expected to arise as a result of dispersion or other non-electrostatic interactions. Within a given charge type, the exact nature of the hydrophile appears to play a minor role in adsorption. It is sometimes found that increasing the hydrated size of the hydrophile will lead to an increase in the efficiency of adsorption by the ion exchange and ion pairing mechanisms.

Once the variable of surfactant charge has been fixed, the nature of the hydrophobe becomes the major factor determining the adsorption characteristics of the system. It has generally been found that within a homologous series of surfactants, an increase in the length of the hydrophobic chain will result in an increase in the efficiency of adsorption. The usual explanation is that as the chain length increases, the free energy gain associated with the removal of the hydrophobe from its aqueous environment and chain-chain interactions among neighboring molecules become more favorable. Some adsorption efficiencies calculated from literature data are given in Table 12.2.

When a phenyl or other aromatic group is added to the hydrophobic chain of a surfactant, it will contribute an effect equivalent to approximately 3.5 methylene groups to the free energy of adsorption. If cationic sites are present on the surface, the phenyl and presumably other aromatics groups such as naphthalene can be induced to interact by induced dipolar forces, resulting from the polarization of the aromatic π -electrons by the positive charge. Such forces will, of course, be much weaker than direct interaction between opposite charges, but they can significantly alter the mode of orientation from a molecular standpoint.

Short alkyl branches on the hydrophobic group can have some effect on adsorption efficiency. Carbon atoms on short branches of an alkyl hydrophobe, those located between two hydrophilic groups, or those on the shorter portion of an alkyl chain with the hydrophile not substituted in the terminal position all seem to contribute an effect equal to half that of the same number of carbons in a normal chain hydrophobe and terminally substituted hydrophile.

The efficiency of surfactant adsorption can quite often be predicted for various changes in the nature of the surfactant, in much the way adsorption at L/V interfaces was treated in Chapter 5. The effectiveness of adsorption, on the other hand, may increase, decrease, or remain unchanged as a result of those same changes. The effect of an increase in the chain length of the hydrophobe,

Table 12.2 The adsorption efficiency (as $-\log C_0$) of some typical surfactants on various substrate types.

Surfactant	Substrate	Temperature (°C)	pH (I.S. ^a)	$-\log C_0$
<i>n</i> -C ₈ H ₁₇ SO ₄ Na	AgI	20	3 (0.001 M)	2.60
<i>n</i> -C ₁₀ H ₂₃ SO ₄ Na	AgI	20	3 (0.001 M)	3.89
<i>n</i> -C ₁₂ H ₂₅ SO ₄ Na	AgI	20	3 (0.001 M)	4.50
<i>n</i> -C ₁₄ H ₂₉ SO ₄ Na	AgI	20	3 (0.001 M)	5.15
<i>n</i> -C ₁₀ H ₂₃ SO ₄ Na	AgI	20	3 (0.0015 M)	3.40
<i>n</i> -C ₁₂ H ₂₅ SO ₄ Na	AgI	20	3 (0.0015 M)	4.38
<i>n</i> -C ₁₄ H ₂₉ SO ₄ Na	AgI	20	3 (0.0015 M)	4.78
C ₁₂ H ₂₅ C ₆ H ₄ SO ₃ Na	AgI	20	3 (0.0015 M)	4.84
<i>n</i> -C ₁₀ H ₂₃ SO ₄ Na	α -Al ₂ O ₃	25	7.2 (0.002 M)	2.75
<i>n</i> -C ₁₂ H ₂₅ SO ₄ Na	α -Al ₂ O ₃	25	7.2 (0.002 M)	3.55
<i>n</i> -C ₁₄ H ₂₉ SO ₄ Na	α -Al ₂ O ₃	25	7.2 (0.002 M)	4.25
<i>n</i> -C ₁₆ H ₃₃ SO ₄ Na	α -Al ₂ O ₃	25	7.2 (0.002 M)	5.00
<i>n</i> -C ₁₀ H ₂₃ NH ₃ OAc	SiO ₂	25	6.7	1.75
<i>n</i> -C ₁₂ H ₂₅ NH ₃ OAc	SiO ₂	25	6.7	2.60
<i>n</i> -C ₁₄ H ₂₉ NH ₃ OAc	SiO ₂	25	6.7	3.45
<i>n</i> -C ₁₆ H ₃₃ NH ₃ OAc	SiO ₂	25	6.7	4.30
<i>n</i> -C ₁₈ H ₃₇ NH ₃ OAc	SiO ₂	25	6.7	5.15

^a I.S., ionic strength.

for example, will depend on the orientation of the adsorbed molecules on the surface. If adsorption is perpendicular to the substrate surface, in an approximately close-packed array, an increase in the chain length of a normal alkane will not result in any significant change in the number of moles of surfactant adsorbed per unit area of surface at saturation. Since the cross-sectional area of a perpendicularly adsorbed, straight-chain molecule does not change much with an increase in the number of units in the chain, the absence of a change in adsorption effectiveness is not a surprising result. In addition, the cross-sectional area of most adsorbed hydrophilic groups is greater than that of normal-chain hydrophobic groups and is therefore the limiting factor in determining the number of surfactant molecules that can be adsorbed per unit area of surface.

If the mode of adsorption is less than perpendicular (L's or trains), or if the molecules are slightly tilted, there may be some increase in the effectiveness of adsorption as the length of the alkyl chain is increased. Again, such an effect is not surprising when one considers that greater dispersion force interaction resulting from a larger alkyl group can lead to greater lateral interactions among surfactant molecules, making possible a greater packing density for the longer chains. A similar effect may be seen when one considers the density, surface tension, cohesive energy density, and many other properties of the homologous series of *n*-alkanes from C₈ to C₁₈ (Figure 12.13).

If the orientation of surfactant hydrophobes is parallel to the surface (in trains, for example), as may occur with materials that have two hydrophilic groups at either end of the molecule or contain aromatic groups that can be polarized, then the effectiveness of adsorption may be found to decrease as the chain length is increased. In a parallel orientation, a greater chain length will

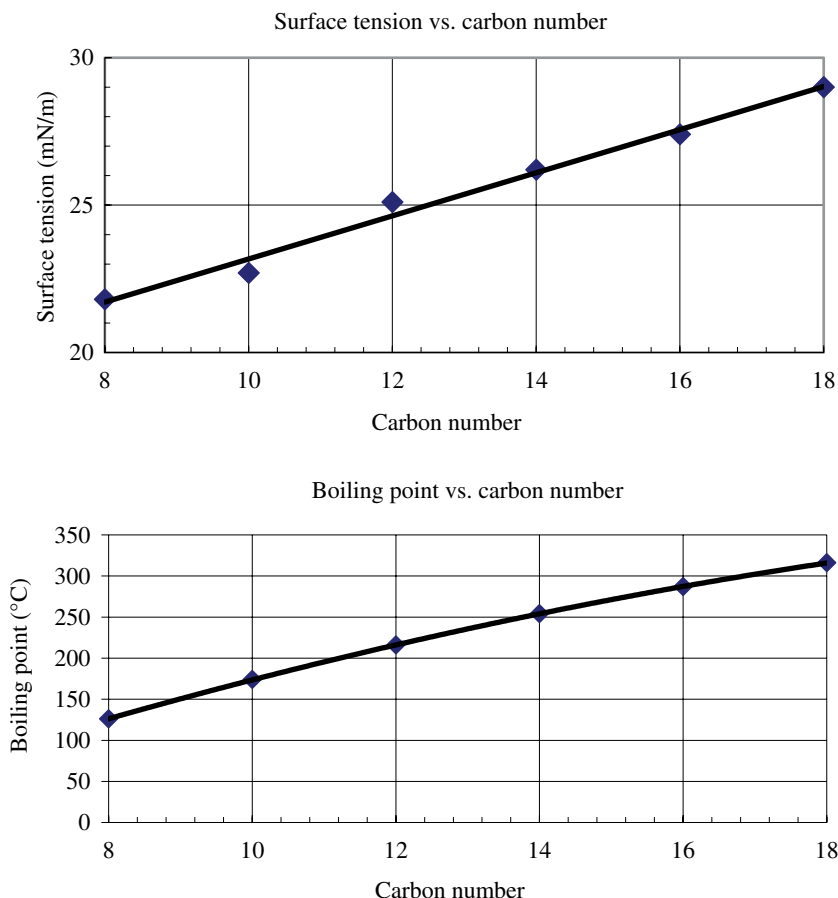


Figure 12.13 Typical variations in surface tension and boiling point for *n*-alkanes as a function of carbon number.

obviously increase the area per molecule required by the adsorbed molecule, and full surface coverage will be attained by the adsorption of fewer moles of surfactant.

While the adsorption of charged surfactants onto charged surfaces is relatively straightforward, that of nonionic species requires a bit more flexibility in interpretation. Such materials may adsorb by mechanisms significantly different from those operative in the case of ionic materials. In general, charged surfaces that also contain hydroxyl and carboxyl groups will adsorb nonionic surfactants by hydrogen bonding or by the acid–base type of interaction between the surface group and oxygen atoms in the nonionic hydrophile. Solid surfaces that contain metal oxides such as silica can interact in the opposite sense, that is, with the surface oxygen serving as the acceptor or base in the interaction.

By far the most common nonionic hydrophile is the polyoxyethylene chain. Although there has not been a great deal published concerning the adsorption of these materials at solid surfaces, it appears that the systems are very sensitive to the length of the ethylene oxide chain. Materials with relatively short POE chains tend to follow Langmuir-type adsorption isotherms in which both the efficiency and the effectiveness of adsorption decrease as the chain length is increased. Those with

intermediate chains are found to adsorb by multilayer formation, while the materials containing longer chains tend not to adsorb at all.

In much the same way that changes in pH can affect the adsorption characteristics of a solid surface, so the extent and manner of adsorption can be altered by changing the nature of the surfactant molecules, especially those containing weak acid or basic groups such as carboxylic acids, non-quaternary ammonium compounds, and amphoteric molecules. In such cases, changes in solution pH may convert the surfactant from an ionic species capable of binding by ion exchange or ion binding mechanisms, to an uncharged material that can interact only through hydrogen bonding, acid–base, or dispersion forces. Solution pH changes can also alter the adsorption characteristics of nonionic surfactants containing POE or other linkages that can be protonated at low pH. At low pH, the ether linkages in POE-containing surfactant materials, in sugars, and in polyglycidols can be protonated to yield positively charged sites that will bind strongly with negative sites on the solid surface.

12.5.2 Adsorption by Uncharged, Polar Surfaces

Adsorption onto polar, uncharged surfaces occurs primarily through hydrogen bonding, acid–base, and dispersion force interactions. Any hydrogen bonding or acid–base interactions between surfactant and solid surface require that the hydrophile contains a group capable of participating in such interactions. For example, head groups that are derivatives of strong acids or bases such as sulfonic acid salts, sulfate esters, and quaternary ammonium ions would not be expected to rely greatly on such mechanisms for adsorption. Groups such as carboxylic acids, on the other hand, can interact with materials containing basic surface groups such as polyesters and polyamides. If the solid surface has —OH or —NH groups that can act as proton donors, it can interact with ether linkages such as in polyoxyethylene. Under some circumstances, the adsorption of nonionic POE surfactants onto polyesters and polyamides exceeds that of anionic materials by more than a factor of 2. Nonionic surfactants derived from straight-chain alcohols and POE are found to adsorb onto surfaces such as cotton in a close-packed monolayer with the molecules parallel to the substrate surface. It is also usually found that if the length of the POE chain is increased, both the efficiency and the effectiveness of adsorption decreases. An increase in the length of the hydrophobic chain, on the other hand, produces an enhancement in the efficiency of adsorption.

Because of the lack of charge groups in the polar materials, such factors as pH and electrolyte content would be expected to have a less pronounced effect upon adsorption than in the case of charged surfaces. At extremes of pH, however, there always exists the possibility of producing charges through the protonation of —OH , —NH , or SiOH groups. In addition, the presence of high concentrations of neutral electrolytes, while having no effect in the sense of electrostatic or electrical double-layer interactions, may decrease the solubility of a surfactant and increase its interactions with the solid surface.

12.5.3 Surfactants at Nonpolar, Hydrophobic Surfaces

Because of the nature of nonpolar, hydrophobic surfaces, initial adsorption will occur almost exclusively by dispersion interactions between the surface and the hydrophobic tail of the surfactant. The orientation of the adsorption, therefore, will be with the tail on the surface and the hydrophile directed toward the solution. The efficiency and effectiveness of adsorption will be largely dependent on the size and nature of the hydrophobe, with a lesser role being played by

the hydrophile. Particularly important from the hydrophilic standpoint will be the extent of mutual repulsion among neighboring head groups, which may affect both the efficiency and the effectiveness of adsorption. Any condition that affects the magnitude of such electrostatic interactions – high electrolyte content, for example – will also be expected to alter adsorption in charged surfactant systems. In the case of nonionic surfactants, where electrostatic interactions are absent, and the materials normally consist of multicomponent mixtures, the role of the head group in determining the form of the adsorption isotherm is more complicated. In fact, the adsorption process for nonionic POE surfactants may act as a form of chromatography in that selected components in the mixture may be adsorbed, leaving a solution of distinctly different character.

As might be expected, the nature of the hydrophobic group – that is, the degree of branching, unsaturation, polar substitution, the presence of aromatic groups, etc. – will play a major role in the ultimate adsorption characteristics of the system, primarily as a result of its effects on the conformation of the hydrophobic chain and its interaction with the solvent and the solid surface. Because of the relatively weak forces operative in nonpolar adsorption processes, it might be expected that the removal of species adsorbed in that way would be relatively easy. In fact, complete desorption in such systems usually is exceedingly difficult, and heroic measures are required to ensure complete removal of the surfactant.

12.6 Surfactant Adsorption and the Character of Solid Surfaces

When a surfactant is adsorbed onto a solid surface, its effect on the character of that surface will depend largely on the dominant mechanism of adsorption. For a highly charged surface, if adsorption is a result of ion exchange, the electrical nature of the surface will not be altered significantly, although its wetting characteristics relative to water may be altered. If, on the other hand, ion pairing becomes important, the potential at the Stern layer will decrease until it is completely neutralized. In a dispersed system stabilized by electrostatic repulsion, such a reduction in surface potential will result in a loss of stability and eventual coagulation or flocculation of the particles.

In addition to the electrostatic consequences of specific charge–charge interactions, surfactant adsorption by ion exchange or ion pairing results in the orientation of the molecules with their hydrophobic groups toward the aqueous phase; therefore, the surface becomes more hydrophobic and less easily wetted by that phase. Once the solid surface has become hydrophobic, it is possible for adsorption to continue by dispersion force interactions. When that occurs, the charge on the surface will be reversed, acquiring a charge opposite in sign to that of the original surface, because the hydrophilic group will now be oriented toward the aqueous phase (Figure 12.14). In a system normally wetted by water, the adsorption process reduces the wettability of the solid surface, making its interaction with other less polar phases (e.g. air) more favorable. Industrially, the production of a hydrophobic surface by the adsorption of surfactant lies at the heart of the froth flotation process for mineral ore separation. Because different minerals have different surface charge characteristics, leading to differences in adsorption effectiveness and efficiency, it becomes possible to obtain good separation by the proper choice of surfactant type and concentration.

Charge reversal cannot, of course, occur on adsorption of nonionic surfactants. However, the character of the surface can be altered significantly with respect to its wettability by aqueous or nonpolar liquids.

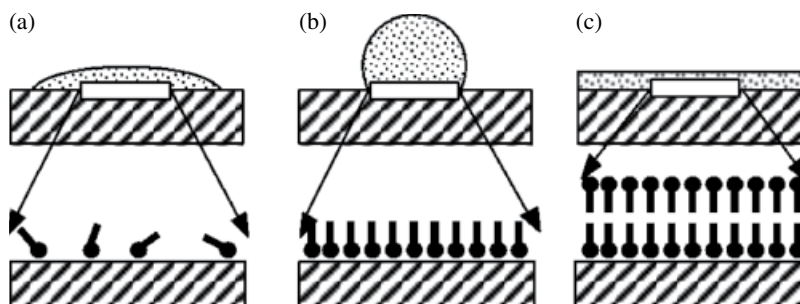


Figure 12.14 Surface charge reversal by surfactant adsorption (a) native surface (charges omitted for clarity), (b) complete surface charge neutralization, and (c) in excess of surfactant, charge reversal by bilayer adsorption.

The adsorption of surfactants onto a clean nonpolar surface must occur with the hydrophilic group oriented outward into the aqueous phase. Adsorption, therefore, will always result in an increase in the hydrophilic character of the surface. Such action is responsible for the generally increased dispersibility of materials such as carbon black in aqueous surfactant systems and the stability of aqueous latex polymers in paints. The action of surfactant adsorption onto colloidal surfaces can be useful to destabilize as well as stabilize systems. It may be useful, for example, to “break” an aqueous dispersion, to isolate the dispersed material, or to facilitate the process of separating dispersed solids in the sewage treatment process, although polymers and polyvalent cation salts are most commonly employed in such instances because of their ability to “bridge” between particles and their dramatic effects on the electrical double layer, as well as their lower cost.

Although surfactant adsorption and its effect on solid surface properties often are discussed in terms of colloidal systems, the same results can be of technological importance for macro-surfaces, especially in the control of the wetting or non-wetting properties of materials in waterproofing, detergency, lubrication, the control of fluid flow through porous media (crude oil production), and corrosion control. Almost any process or product that involves the interaction of a solid and a liquid phase will be affected by the process of surfactant adsorption; thus, the area represents a major segment of the technological application of surfactants.

12.7 Wetting and Related Phenomena

As indicated in the preceding sections, the adsorption of surfactants at solid–liquid interfaces can play a significant role in determining the nature of the interactions between solvent and solid and among solid surfaces, especially as related to such a phenomenon as colloidal stability. A similar role can be played by surfactants on essentially infinite surfaces related to wetting, spreading, adhesion, and lubrication. Although the basic phenomena are the same for the wetting of extended surfaces and the stabilization of colloidal particles, a number of concepts are more uniquely applied to the more extended surfaces.

While the term “wetting” may conjure up a fairly simple image of a liquid covering a surface, from a surface chemical standpoint, the situation is somewhat less clear-cut. Three classes of wetting phenomena can be defined based on the physical process involved. They are adhesion,

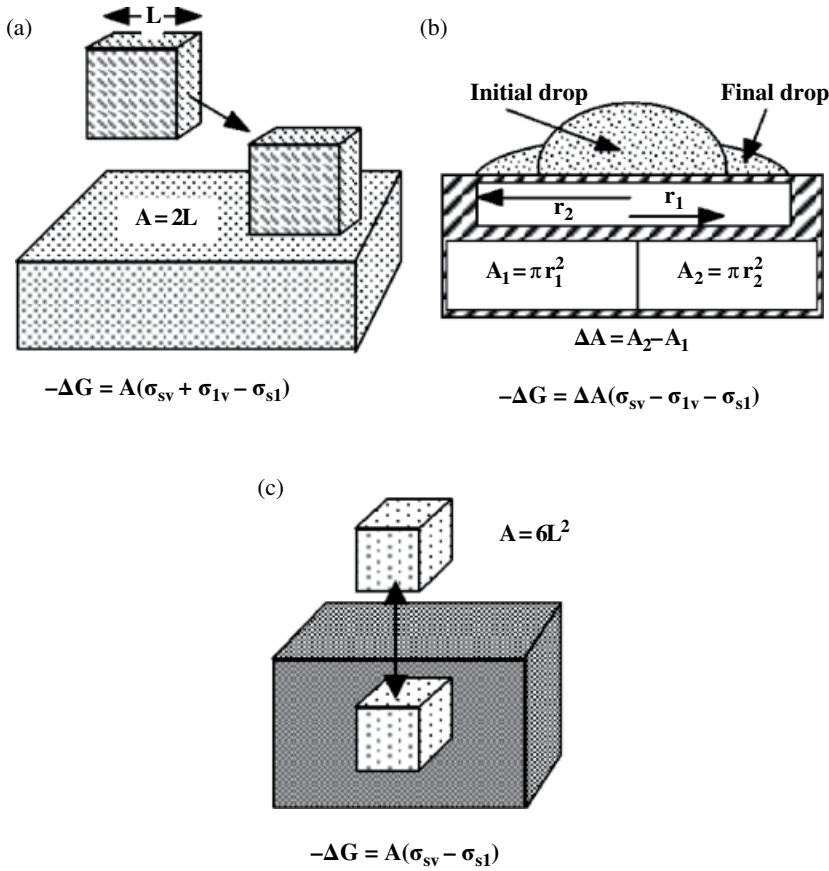


Figure 12.15 Schematic representations of important wetting processes (a) adhesion, (b) spreading, and (c) immersion.

spreading, and immersion (Figure 12.15). The distinctions among the three may seem subtle, but they can be significant from a thermodynamic and phenomenological point of view.

“Adhesion wetting” refers to the situation in which a solid, previously in contact with a vapor phase, is brought into contact with a liquid phase. During the process, a specific area of solid–vapor interface, A , is replaced with an equal area of solid–liquid interface (Figure 12.15a). The free energy change for the process is given by

$$-\Delta G = A(\sigma_{SA} + \sigma_{LA} - \sigma_{SL}) \quad (12.4)$$

where the σ ’s refer to the solid–air (SA), liquid–air (LA), and solid–liquid (SL) interfacial energies. The quantity in parentheses in Eq. (12.4) is known as the thermodynamic work of adhesion, W_a , and the equation is that of Dupré. From the equation, it is clear that any decrease in the solid–liquid interfacial energy σ_{SL} will produce an increase in the work of adhesion (and a greater energy decrease), while an increase in σ_{SA} or σ_{LA} would reduce the energy gain from the process.

Spreading applies to the situation in which a liquid (L_1) and the solid are already in contact and the liquid spreads to displace a second fluid (L_2 , usually air) as illustrated in Figure 12.15b. During

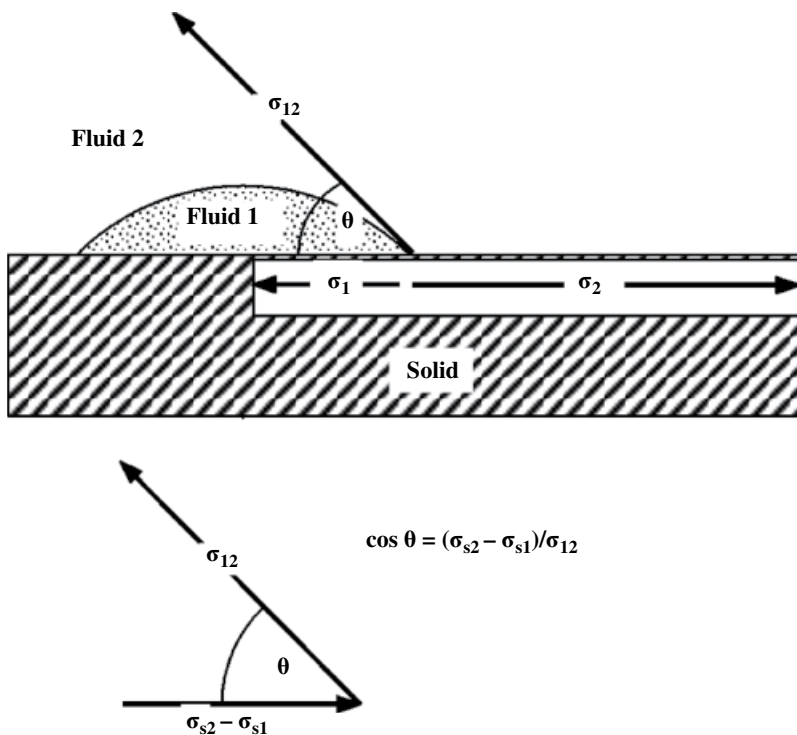


Figure 12.16 Schematic illustration of the mechanical equilibrium of surface forces leading to contact angle formation as given by Young's equation.

the spreading process, the interfacial area between solid and L_2 is decreased by an amount A , while that between the solid and L_1 increases by an equal amount. The interfacial area between L_1 and L_2 also increases during the process. The change in interfacial area in each case will be the same, so that the total decrease in the energy of the system will be

$$-\Delta G = A(\sigma_{SL2} - \sigma_{SL1} - \sigma_{12}) \quad (12.5)$$

where σ_{12} is the interfacial tension between fluids 1 and 2. If the term in parentheses, defined as the spreading coefficient, S , (see Chapter 11) is positive, then L_1 will spontaneously displace L_2 and spread completely over the surface (or to the greatest extent possible). If S is negative, the spreading process as written will not proceed spontaneously.

In a system in which a liquid is spreading over a second liquid phase, it is possible to directly measure the values for computing the value of S . When a solid surface is involved, the value of σ_{SL2} is not directly available from experiment, so an indirect route must be found to evaluate the interactions among the three-component phases. The approach normally taken for such a determination is to measure the contact angle, θ , which the liquid makes with the solid of interest.

Figure 12.16 shows the general diagram for the contact angle of a liquid L_1 on a solid substrate in the presence of a second fluid L_2 . At equilibrium, the contact angle measured through the liquid drop (L_1) is related to the interfacial energies between the various components through Young's equation:

$$\sigma_{1/2} \cos \theta = \sigma_{SL2} - \sigma_{SL1} \quad (12.6)$$

or

$$\cos \theta = (\sigma_{SL2} - \sigma_{SL1}) / \sigma_{1/2} \quad (12.7)$$

A combination of Eq. (12.7) and the equation for the spreading coefficient S gives

$$S = \sigma_{12} (\cos \theta - 1) \quad (12.8)$$

It is clear from Eq. (12.8) that for $\theta > 0$, S cannot be positive or zero, and spontaneous spreading will not occur.

The third type of wetting, immersion wetting, covers the situation in which a solid substrate not previously in contact with a liquid is completely immersed in liquid L_1 , completely displacing all solid– L_2 interface (Figure 12.15c). In this case, the free energy change at equilibrium is determined by two factors, the component related to the solid–air interface $A\sigma_{SL2}$ and that of the solid–liquid interface $A\sigma_{SL1}$, where A is the total surface area of the solid. The free energy change is then given by

$$-\Delta G = A(\sigma_{SL2} - \sigma_{SL1}) \quad (12.9)$$

From these relationships for wetting processes, it is clear that the interfacial energies between a solid and any contacting liquid and the interfacial tension between the liquid and the second fluid (usually air) control the manner in which the system will ultimately perform. The ability to alter one or several of those surface energy components makes it possible to manipulate the system to attain the wetting properties desired for a given system. It is through the action of surfactants at any or all of those interfaces that such manipulation is usually achieved. We now turn our attention more specifically to the role of surfactant structure in the alteration and control of the wetting process.

12.7.1 Surfactant Manipulation of the Wetting Process

Because of its high surface tension ($\approx 72 \text{ mN/m}$) relative to most covalent solids (see Table 12.1), water does not spontaneously spread or wet most such materials. As pointed out earlier, for such spreading to occur, the spreading coefficient S must be positive; that is, $\sigma_{SL2} > (\sigma_{SL1} + \sigma_{12})$ (from Eq. (12.5)). The addition of a surfactant to lower the surface tension of the aqueous phase σ_{12} and possibly σ_{SL1} will often result in improved wetting of the solid substrate. Such will not always be the case, however. As discussed above, a surfactant may adsorb onto a solid surface with one of several molecular orientations, the predominant ones being with the head group pointing into the solution phase or with the head group intimately associated with a surface group on the solid. If the orientation is with the head group exposed, the value of σ_{SL1} as well as σ_{12} will be reduced, and S will become more positive. If the surfactant is oriented with the hydrophobic tail exposed, σ_{SL1} will be increased, and spreading wetting will become less favored.

The penetration of water into a porous solid or fabric can also be variously affected by the lowering of σ_{12} by surfactant addition. The equation for the pressure forcing the penetration of liquid into capillaries due to surface curvature is

$$\Delta P = 2\sigma_{12} \cos \theta / r = 2(\sigma_{SL2} - \sigma_{SL1}) / r \quad (12.10)$$

where r is the effective radius of the capillary and θ is the contact angle of the liquid at the S/L₁/L₂ three-phase contact line. For $\theta > 0$, the value of ΔP will depend on the relationship $\sigma_{SL2}-\sigma_{SL1}$, so any change in the surface tension σ_{12} that is not accompanied by a change in σ_{SL1} will result only in an increase in $\cos \theta$. The lowering of the liquid surface tension will not change ΔP and therefore will not affect pore penetration. If, on the other hand, $\theta = 0$, Eq. (12.10) reduces to

$$\Delta P = 2\sigma_{12}/r \quad (12.11)$$

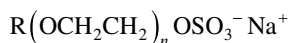
and any reduction of σ_{12} will reduce the pressure leading to liquid penetration.

It should be fairly obvious from the foregoing discussions of the complexities of surfactant adsorption and wetting phenomena that clear, totally unambiguous rules relating surfactant structure to its effects on wetting are difficult to define. Each specific case must be considered carefully to ensure that the effects of the various possible interfacial interactions are incorporated. As mentioned in Chapter 10, one method for correlating surfactant structure with wetting characteristics is through the use of the hydrophile–lipophile balance (HLB). As a rule of thumb, surfactants with HLB numbers in the intermediate range of 7–9 exhibit better wetting characteristics for aqueous solutions on most solid surfaces than those with higher or lower values. As so often in the area of surfactant activity, however, due care must be taken in trying to apply even the simplest such rules.

Perhaps the most widely used test for the evaluation of the wetting power of surfactant is the Draves wetting test in which a piece of cotton cloth with appropriate weights attached is placed on the surface of a surfactant solution and the time for complete wetting or submersion of the sample at a given surfactant concentration, temperature, electrolyte content, etc. is determined. A standard set of conditions for the test is water of low ionic strength (<300 ppm Ca^{2+}) at 25°C and a surfactant concentration of 0.1% by weight. Typical wetting times for several common surfactants are given in Table 12.3. Similar tests have been developed for the wetting of powders.

From the data in the literature, it appears that optimal wetting characteristics are obtained when a normal-chain hydrophobic group has a length of 12–14 carbons. Variations in structure that alter the effective chain length for most surface-active properties will also be reflected in the wetting properties. Branching in the hydrocarbon chain, for example, reduces the effect of the branched carbons to approximately two thirds of that of unbranched atoms. The optimal chain length for molecules with internally located hydrophilic groups may be increased by one or two carbons. Carbons located between the primary head group and a second polar group will usually contribute approximately half of the effect seen for similar groups in the main chain.

It has been found that surfactants with symmetrically located internal head group substitution and ortho-substituted alkylbenzene sulfonates are better wetting agents than their straight-chain and para-substituted analogues. The enhanced wetting activity of the nonlinear materials is generally associated with their more compact structure, allowing for faster diffusion to the solid–liquid interface and greater relative adsorbing efficiency. The presence of additional polar groups in the molecule (e.g. ester and amide linkages and POE chains) usually results in a decrease in wetting power. It has been found that in a series of surfactants with the general structure



where R is $\text{C}_{16}\text{H}_{33}$ or $\text{C}_{18}\text{H}_{37}$ and $n = 1-4$, the Draves wetting time increased with each added OE group.

Nonionic surfactants such as POE alcohols and fatty acids will generally pass through a minimum in wetting power, as determined by the Draves test, as the length of the POE chain is increased. For a given hydrophobic chain length, the maximum in wetting will occur for the POE

Table 12.3 Wetting times for several common surfactants.

Surfactant	Concentration (wt. %)	Wetting time (seconds)	
		Water	300 ppm Ca ²⁺
<i>n</i> -C ₁₂ H ₂₅ SO ₄ ⁻ Na ⁺	0.025	>300	—
<i>n</i> -C ₁₂ H ₂₅ SO ₄ ⁻ Na ⁺	0.05	39.9	—
<i>n</i> -C ₁₂ H ₂₅ SO ₄ ⁻ Na ⁺	0.10	7.5	—
<i>sec-n</i> -C ₁₄ H ₂₉ SO ₄ ⁻ Na ⁺	0.063	19.4	—
<i>sec-n</i> -C ₁₅ H ₃₁ SO ₄ ⁻ Na ⁺	0.063	14.0	—
<i>sec-n</i> -C ₁₆ H ₂₃ SO ₄ ⁻ Na ⁺	0.063	22	—
<i>sec-n</i> -C ₁₇ H ₃₅ SO ₄ ⁻ Na ⁺	0.063	25	—
<i>sec-n</i> -C ₁₈ H ₃₇ SO ₄ ⁻ Na ⁺	0.063	39	—
C ₁₂ H ₂₅ C ₆ H ₄ SO ₃ ⁻ Na ⁺	0.125	6.9	—
<i>n</i> -C ₁₀ H ₂₁ CH(CH ₃)C ₆ H ₄ SO ₃ ⁻ Na ⁺	0.10	10.3	80
<i>n</i> -C ₁₂ H ₂₅ CH(CH ₃)C ₆ H ₄ SO ₃ ⁻ Na ⁺	0.10	30	>300
<i>n</i> -C ₁₄ H ₂₉ CH(CH ₃)C ₆ H ₄ SO ₃ ⁻ Na ⁺	0.10	155	>300
<i>p-t</i> -C ₈ H ₁₇ C ₆ H ₄ (OCH ₂ CH ₂) ₅ OH	0.05	25	—
<i>p-t</i> -C ₈ H ₁₇ C ₆ H ₄ (OCH ₂ CH ₂) ₈ OH	0.05	25	—
<i>p-t</i> -C ₈ H ₁₇ C ₆ H ₄ (OCH ₂ CH ₂) ₉ OH	0.05	25	—
<i>p-t</i> -C ₈ H ₁₇ C ₆ H ₄ (OCH ₂ CH ₂) ₁₀ OH	0.05	30	—
<i>p-t</i> -C ₈ H ₁₇ C ₆ H ₄ (OCH ₂ CH ₂) ₁₂ OH	0.05	50	—

chain length for which the cloud point lies just above the test temperature. As a rule, POE nonionic surfactants with an effective hydrophobic chain length of approximately 11 methylene units and POE chain length of 6–8 will exhibit optimal wetting power. In addition, POE alcohols and thioethers are generally found to be superior to equivalent POE fatty acids.

A number of external factors that can affect the wetting power of surfactants include temperature, electrolyte content, pH, and the addition of polar organics and co-surfactants. An increase in solution temperature, for example, will generally reduce the wetting power of most ionic surfactants, presumably as a result of greater solubility and a reduced tendency for adsorption at interfaces. The optimal chain length for maximum wetting in a given surfactant series, therefore, increases with the temperature.

The addition of electrolyte will alter wetting characteristics by altering the solution properties of the surfactant. Electrolytes that cause a reduction in the **cmc** of a surfactant solution will normally produce improvements in wetting power. For example, surfactants with short hydrophobic tails that would show relatively poor wetting characteristics in distilled water will usually exhibit better performance in concentrated electrolyte solutions.

The addition of long-chain alcohols and nonionic co-surfactants has been reported to increase the wetting properties of many anionic surfactants. In the case of cationic surfactants, the presence of POE nonionic materials may reduce wetting power as a result of weak complex formation between the POE chain and the cationic group and a consequent reduction of the rate of diffusion of the surfactant to the interface.

Solution pH becomes important to wetting characteristics primarily (and not surprisingly) when weakly acidic or basic groups are present in the surfactant molecule. A prime example is that of the α -sulfocarboxylic acids, which show generally better wetting behavior at low pH where the carboxyl group is not ionized.

12.7.2 Some Practical Examples of Wetting Control By Surfactants

The wetting of solid surfaces plays an important role in many technologically important processes, and an understanding of the part played by surfactants in such processes can go a long way toward solving the problem of choosing the proper material for the job. The following sections illustrate some of the principles involved by means of a brief discussion of a few of the most important processes entailing the action of surfactants at solid-liquid interfaces.

12.7.3 Detergency and Soil Removal

Detergency is unquestionably a surface and colloidal phenomenon reflecting the physicochemical behavior of matter at interfaces. Since the field is concerned principally with the removal of complex mixtures of soils and oily mixtures from equally complex solid substrates, it is not surprising that such systems do not lend themselves readily to analysis by the more fundamental theories of surface and colloid science. A rigorous treatment of the current status of detergency theory would constitute a book itself. This section summarizes some of the most important aspects of detergency and illustrates how the chemical structure of the surfactants and other components in a formulation can affect overall performance.

12.7.4 The Cleaning Process

The cleaning of a solid substrate involves the removal of unwanted foreign material from its surface. In this case the term “detergency” is restricted to systems having the following characteristics: (i) the cleaning process is carried out in a liquid medium; (ii) the cleaning action is a result primarily of interfacial interactions among the soil, substrate, and solvent system; and (iii) the primary process is not solubilization of the soil in the liquid phase, although that may play a minor role in the overall detergent action. Mechanical agitation and capillary action are also important aspects of the overall detergency process, especially when modern stain removal treatments are applied.

While most detergent-related applications are carried out in aqueous systems, the important nonaqueous “dry” cleaning systems also fulfill the foregoing requirements for detergency. In the following discussion, however, all references are to water as the solvent unless noted otherwise.

In detergency, as in many important technical processes, the interaction between solid substrates and dissolved or dispersed materials is of fundamental importance. Surfactants, as a class of materials that preferentially adsorb at several types of interfaces because of their amphiphilic structure, naturally play an important role in many such processes. In most adsorption processes related to detergency, it is the interaction of the hydrophobic portion of the surfactant molecule with the dispersed or dissolved soil and with the substrate that produces detergent action. Such adsorption alters the chemical, electrical, and mechanical properties of the various interfaces and depends strongly upon the nature of each component. In the cleaning of textile materials with anionic surfactants, for example, the adsorption of the surfactant onto the fabric and the soil

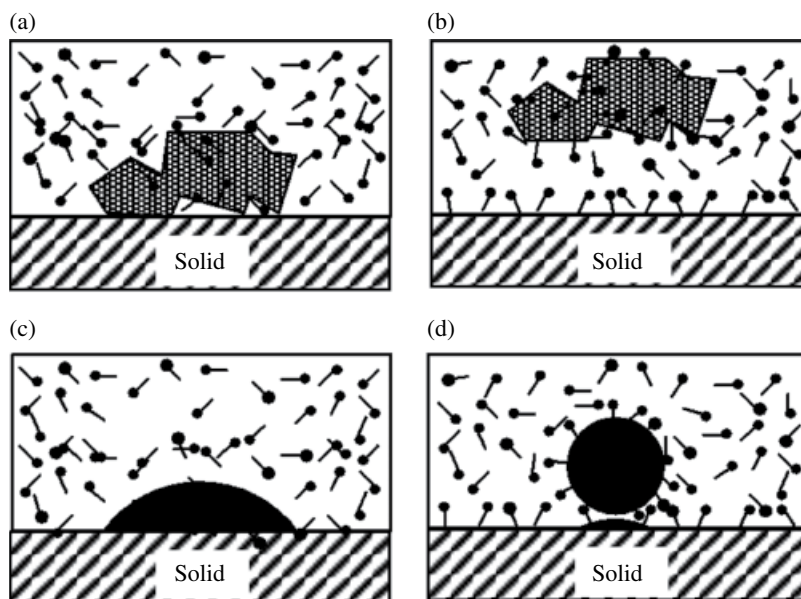


Figure 12.17 A general mechanism for solid soil removal through surfactant action (a) solid dirt removal and (b) oily dirt removal.

introduces electrostatic repulsive interactions that tend to reduce the adhesion between soil and fiber, lifting the soil and retarding re-deposition. The process is illustrated schematically in Figure 12.17. With nonionic surfactants, the mechanism is less clear-cut; however, steric repulsion between adsorbed surfactant layers and solubilization is of primary importance.

12.7.5 Soil Types

In general, there are two types of soil encountered in detergency situations: liquid, oily substances, and solid particulate material. Many stains on textiles such as blood, wine, mustard, catsup, and the like involve proteins, carbohydrates, and relatively high molecular weight pigment-like materials that pose special problems in terms of the interfacial interactions involved. The interactions of each class of soil or stain with the solid substrate can be quite complex, and the mechanisms of soil removal may be correspondingly complex.

Solid soils may consist of various mineral compositions, carbon (soot) having a variety of surface characteristics, metal oxides and pigments, etc. Liquid soils may contain skin fats (sebum), fatty acids and alcohols, vegetable and mineral oils, synthetic oils, and liquid components of creams and cosmetics. As with the solid soils, the surface chemical characteristics of the liquid soils can vary widely. It is not surprising, then, that the derivation of a comprehensive theory for detergency that can characterize every situation poses a challenge. There are some basic similarities between the two soil types, however, which allow for some generalization, while each class will also have its special requirements for efficient detergency.

The adhesion of both solid and liquid soils to solid substrates will, to a greater or lesser extent, result from dispersion and van der Waals interactions. Adsorption due to other polar forces such as acid-base interactions or hydrogen bonding is also usually of minor importance except where highly polar soils and substrates are involved. Adhesion by electrostatic interactions is generally

less important for liquid soil systems, but it can become important, and in fact, determining, in the cases of some mineral and biological soils. When electrostatic forces are involved, resulting soil stain can be very difficult to remove by normal cleaning processes.

Where soil adsorption predominantly is a result of dispersion and van der Waals interactions, nonpolar materials such as carbons and hydrocarbon oils can be especially difficult to remove from hydrophobic surfaces such as polyesters. More hydrophilic soils such as clays, fatty acids, etc., on the other hand, can be more difficult to remove from hydrophilic surfaces such as cotton. Mechanical forces can also inhibit cleaning action, especially in fibrous materials with particulate soils, as a result of entrapment of the particles in the fibers. It is obvious, then, that the cleaning process can be extremely complex, and optimum results may be possible only for specifically defined systems. Like the universal solvent, the universal detergent is, in all likelihood, beyond our technological reach.

12.7.6 Solid Soil Removal

The removal of solid, particulate soils from a substrate in an aqueous cleaning bath involves the wetting of the substrate and soil by the cleaning bath followed by adsorption of surfactant and/or other components at the substrate–liquid and soil–liquid interfaces (Figure 12.17). The result is (ideally) a reduction of the energy required to separate the two phases and the creation of an electrostatic or steric barrier to retard or prevent re-deposition onto the substrate.

The adhesion of small particles to a substrate may be significantly reduced by immersion in water if the interactions at the interface are favorable, as indicated by the spreading coefficient, S (Eq. (12.5)). The presence of the water brings about the formation of an electrical double layer at each S/L interface. If both soil and substrate are negatively charged, electrostatic repulsion will reduce or eliminate adhesion forces and lead to soil removal. In addition, the presence of water may cause the substrate to swell, further reducing soil–substrate interactions. In many instances, however, the surface forces embodied in the spreading coefficient for water alone are not sufficient to bring about particle–substrate separation. The addition of surfactant can improve the situation in the ways already mentioned, but it is often found that vigorous mechanical action is necessary to make the kinetics of the process acceptable.

It is interesting to note that most commonly encountered solid soils are minerals, which usually carry a net native negative surface charge in aqueous solution. If cationic surfactants are present in the wash solution, specific adsorption through electrostatic attraction will occur, leading to a less favorable situation for soil removal. It would require the formation of a bilayer of adsorbed surfactant to attain the desired electrostatic effects for efficient removal of the soil and to prevent re-deposition. For that reason, cationic surfactants are seldom encountered in normal cleaning solutions, except where their bactericidal characteristics are required. Their tendency to adsorb onto anionic substrates (especially fabrics) does have its advantages, however. The production of more hydrophobic surfaces through such adsorption lies behind the utility of cationic amphiphiles as fabric softeners. By adsorbing onto the textile fiber surfaces, such materials reduce the friction between the fabric and the contacting skin to produce the desired soft texture. The hydrophobic nature of the adsorbed surface also reduces the effects of static charge buildup giving the material a softer, less irritating feel.

The simple act of dispersing soil particles in the cleaning bath has not been found to ensure effective cleaning. There appears to be little correlation between detergency and dispersing power for most surfactants. For example, surfactants that are excellent dispersing aids are often found to

have poor detergency characteristics and vice versa. Increased adsorption onto the soil and substrate in the cases of anionic and nonionic surfactants appears to correlate well with detergency, however, indicating that the effectiveness of a particular surfactant in the cleaning process is related to its effectiveness at separating the soil and substrate. Some of what is known about the relationships between detergency and surfactant structure is discussed below.

12.7.7 Liquid Soil Removal

Like that for solid soils, the first step in the cleaning of oily soils from a substrate is the separation of the two interfaces. Afterward, the problem becomes that of keeping them apart. The primary mechanism for the soil removal process is generally felt to be the so-called rollback mechanism illustrated in Figure 12.18. In essence, the process involves the penetration of liquid into the soil–substrate interface by capillary action or as a result of mechanical separation. As the cleaning solution penetrates, the adsorption of surfactant at the soil–solution and solid–solution interfaces decreases the adhesive forces between the two, resulting in an increase in the soil–substrate contact angle and, eventually, in displacement of the soil by the cleaning solution.

Once the soil has been separated from the substrate, it is necessary to prevent its re-deposition until it is removed in the rinsing process. There are two general mechanisms for the isolation of oily soils from the substrate: micellar solubilization and emulsification. The solubilization of oily materials in surfactant micelles is probably the most important mechanism for the removal of oily soil from substrates and follows the general tendencies outlined in Chapter 8. It has generally been observed that oily soil removal from textile surfaces becomes significant only above the **cmc** for nonionic surfactants and even for some anionic materials with low **cmc**'s. Removal efficiency

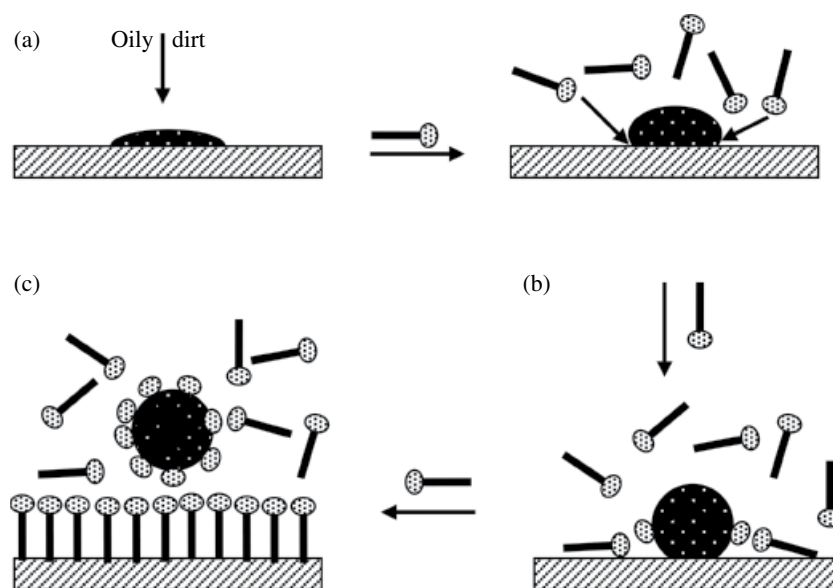


Figure 12.18 The “rollback” mechanism for oily soil removal: surfactant adsorption at O/W and S/W interfaces acts to initiate drop deformation (a), followed by “necking” of the attached drop (b), and eventual detachment (c).

reaches a maximum at several times that concentration. Since the adsorption of surfactants at interfaces involves the monomeric, rather than the micellar form, while solubilization involves only the micellar form, those results would appear to indicate that in these cases, solubilization is more important than adsorption-related effects such as wetting, emulsification, etc., in the overall cleaning process.

The degree of solubilization of oily soils depends on the chemical structure of the surfactant, its concentration in the bath, and the temperature. At low surfactant concentrations, solubilization occurs in small, roughly spherical micelles, and a relatively small amount of oil can be solubilized. At surfactant concentrations well above the **cmc** (10–100 times), larger micellar structures that have a greater solubilizing capacity may be encountered, or some mechanism related to microemulsion formation may take over.

In solutions of some ionic surfactants, the working concentration is often not much above the **cmc**, so solubilization may not be a significant factor in oily soil removal. For nonionic surfactants, the extent of solubilization depends on the temperature of the cleaning solution relative to the cloud point of the surfactant, since solubilization of oily materials increases significantly as the cloud point is approached. This may account in part for the observation that soil removal by nonionic surfactants is often at a maximum at temperatures in the vicinity of the cloud point. When insufficient surfactant is present to solubilize the oily soil, the remainder may be suspended by emulsification.

Since the detergent power of many surfactants cannot be directly related to their efficacy as emulsifiers, there exists some question as to the importance of emulsification as a primary soil removal mechanism and re-deposition control. Certainly, for efficient solubilization to occur, the area of surfactant solution/soil interface must be maximized, which implies a reduction in the solid substrate/oil interface.

A major criticism of the emulsification mechanism is that, since most detergent class surfactants are not particularly good emulsifiers, emulsified soil droplets will be very unstable, resulting in droplet coalescence and significant re-deposition. The rollback process, as well as any possible emulsification processes, will generally be aided by the addition of mechanical energy, although it is doubtful that such added energy would be sufficient to significantly overcome the inherent instability of most detergent–emulsion systems.

12.7.8 Soil Re-deposition

The term “re-deposition” has already been used several times. Because most cleaning processes are “batch” processes, there will always exist the possibility that soils removed from the substrate will be re-deposited onto the surface as a result of a lack of colloidal stability in the dispersed soils. For oily soils removed by solubilization, the process is thermodynamically driven, so it is essentially a one-way street, and re-deposition will be minimal. Solid soils, on the other hand, cannot be solubilized, and re-deposition must be retarded by other kinetically controlled means. Emulsified oily soils, where they occur, must be handled similarly.

One major role of surfactants at solid interfaces is to impart a degree of colloidal stability to finely divided particles in aqueous solutions. The adsorption of ionic surfactants at the soil–water and substrate–water interfaces produces an electrical double layer that retards the mutual approach of the interfaces and prevents or at least hinders re-deposition. Nonionic surfactants perform the same task by the formation of a steric or entropic barrier to approach, although the efficacy of such a mechanism is probably less than the electrostatic repulsions in most aqueous systems.

12.7.9 Correlations of Surfactant Structure and Detergency

Any correlation between the detergent power of a surfactant and its chemical structure will be complicated by the existence of a wide variety of soil types that may have vastly different interactions with a given surfactant type. It is important, therefore, to specify the exact nature of the system when trying to make any general statements concerning such correlations.

For oily soils, where solubilization is the primary mechanism of soil isolation and ultimate removal, it is reasonably safe to say that any structural characteristic of the surfactant molecule that improves its solubilizing capacity as described in Chapter 8 will tend to improve its performance in such systems. Equally, if soil emulsification is important, surfactants with the proper HLB for emulsification would be expected to have advantages over those lying outside the optimum range for a given oil type. It has been reported that nonionic surfactants perform well in the process of removing and preventing the re-deposition of oily soils at lower concentrations than anionic analogues, the reasoning being that their **cmc** is reached at lower concentrations.

As indicated earlier, the orientation of the adsorbed surfactant molecule at the solid–liquid interface will determine the physical result of the adsorption process. In detergency, the surfactant must orient with the hydrophilic head group toward the aqueous phase, or the mechanisms for soil removal and prevention of re-deposition will not be operative. For that reason, the detergent activity of a given surfactant in the system will also depend on the polar or ionic nature of the substrate. Both anionic and nonionic surfactants, for example, may exhibit good detergent properties on relatively nonpolar surfaces such as polyesters and nylons. On cottons and cellulose fibers, which are more hydrophilic, anionic surfactants will usually perform better than nonionic materials. It may reasonably be expected that the greater hydrophilicity of such surfaces leads to substantial polar or hydrogen bonding interactions with the POE units of the surfactant and forces its orientation to expose more of the hydrophobic tail to the aqueous phase or causes the surfactant molecule to lie along the substrate surface (parallel) and thereby reduce the extent of adsorption. Such orientation may increase or at least not sufficiently decrease the interfacial energies at the soil–water and substrate–water interfaces and thereby retard soil removal. As already mentioned, cationic materials are generally less useful than the other types as detergents but are especially so when the substrate has significant anionic character, leading to a reversed molecular orientation and the formation of a substantially hydrophobic surface.

Clearly, the extent and orientation of adsorption of surfactant molecules onto a solid substrate are of primary importance to their action in the detergency process. Therefore, any alterations in molecular structure that affect such adsorption characteristics should be expected also to affect detergent power. As was shown earlier in this chapter, an increase in the length of a hydrocarbon tail will result in an increase in the efficiency with which that material is adsorbed at the solid–solution interface. Similarly, modifications such as branching and internal location of the hydrophilic group will reduce that tendency. It is generally observed, therefore, that maximum detergent activity for a given carbon chain length and head group will be attained with a normal chain and terminal head group location. A number of studies have confirmed that detergent efficiency increases as the length of the hydrophobic tail is increased and as the head group is moved from internal to terminal locations. The limiting factor in all that, of course, is that the tail cannot become so long that low water solubility becomes a problem.

Although straight-chain hydrophobes with terminal head groups produce optimal detergency under ideal circumstances, the presence of electrolytes and polyvalent cations can reduce the solubility of many materials to the extent that their activity is no longer sufficient for the job. In such

situations, it may be found that analogues with the hydrophilic group located internally along the chain will be superior detergents.

The nature of the surfactant head group is important for several reasons, including control of the orientation of surfactant adsorption when charged surfaces are involved and control over the sensitivity of the material to pH, electrolytes, and polyvalent ions. In the case of POE nonionic materials, increases in the length of the POE chain result in a decrease in the efficiency of adsorption on the substrate and a loss in detergent power, all other things being equal. When POE chains are inserted between the hydrophobic tail and an anionic group, such as in POE sulfonates, the material is usually found to be superior in detergent properties to the parent “normal” sulfonate. A number of other trends relating structural characteristics of surfactants to detergency have been determined, but the most generally applicable can be summarized as follows:

- 1) Within the limits of solubility, detergent power increases with the length of the hydrophobic chain.
- 2) For a given number of carbon atoms in the hydrophobic tail, maximum detergency is attained with straight rather than branched chains.
- 3) Terminal positioning of the head group produces superior results within a surfactant series.
- 4) For nonionic surfactants, optimal detergency is obtained when the cloud point of the surfactant lies just above the solution working temperature.
- 5) For POE nonionic surfactants, an increase in the length of the POE chain (once sufficient solubility has been attained) often results in a decrease in detergent power.
- 6) The insertion of a POE chain from three to six units between the hydrophobic tail and the primary ionic head group generally results in superior detergent performance.
- 7) Characteristics of the substrate such as polarity and electrical charge that lead to adsorption via the head group will result in poor detergent action. That is especially the case for cationic surfactants interacting with negatively charged surfaces.

12.7.10 Nonaqueous Cleaning Solutions

Although aqueous systems constitute the major portion of surfactant applications in detergency, nonaqueous or “dry” cleaning processes also constitute an important economic factor. Included in such processes are the familiar dry-cleaning processes as applied to fine fabrics and articles that are adversely affected by water, as well as processes for the cleaning of various metal and ceramic parts that cannot tolerate significant exposure to moisture.

In such applications, solubility of the surfactant in the nonaqueous solvent is obviously the primary requirement. A wide variety of structures have been found useful in such applications, including nonionic materials such as POE alkylphenols, amides, and phosphate esters, sodium dialkylsulfosuccinates, alkylarylsulfonates, and petroleum sulfonates. Although extensive experimental data are not available, it appears that the polar head group of the surfactant in such uses is of primary importance, given a hydrophobic tail sufficient to ensure the proper overall solubility.

Since the solvent system for dry cleaning is nonaqueous, the mechanisms for cleaning action will differ in sense, but not in principle, from those in aqueous detergent systems. In general, there are two processes to consider: (i) the adsorption of surfactant at the solid– or liquid–soil interface in such a way as to lower the solvent/soil interfacial energy and to facilitate removal and inhibit re-deposition and (ii) the solubilization of water-soluble soils in the interior of the reversed micelle. The first process requires that the surfactant adsorbs with the hydrophobic tail oriented outward toward the nonaqueous solvent, the opposite to that necessary for good detergent action in water.

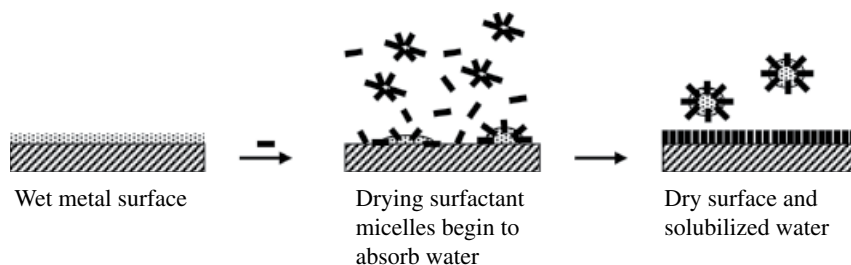


Figure 12.19 Solid surface drying by water solubilization in reversed micelles.

The second step requires that water and accompanying soils have a high affinity for the polar group on the surfactant. For the prevention or retardation of re-deposition, the surfactant depends upon its ability to provide a steric barrier between soil and substrate, suggesting that longer hydrocarbon chains would provide better dry-cleaning action. Similar mechanisms can be invoked in the application of nonaqueous surfactant systems as so-called drying mixtures with which water can be removed from metal surfaces by the solubilizing action of inverted micelles (Figure 12.19).

12.8 Suspensions and Dispersions

The suspension or dispersion of solid particles in liquid media is an immensely important technological process related to many of the major chemical areas, including foods, pharmaceuticals, paints and inks, cosmetics, and agricultural products. The ability to prepare suspensions of the proper particle size and to maintain the stability of such dispersions for extended periods of time quite often involves the use of one or more surfactants. The role of the surfactant may be related to the preparation process or to the long-term stability of the system or both. In any case, the proper choice of surfactant will be important to the ultimate success of the process.

It is usually considered that there are two basic mechanisms for the preparation of solid suspension in liquid media – by condensation, in which the particles are built up from basic molecular units (emulsion polymerization, crystallization, etc.), and dispersion, in which small particles are formed in the suspending liquid by breaking up or grinding larger solid units. In each case, the presence of a surfactant can have a significant effect on the characteristics of the final product.

In condensation processes, the surfactant may be important in all stages of the process from nucleation through particle growth to ultimate stabilization. The exact part played will depend on the details of the system under consideration. In emulsion polymerization, for example, nucleation may occur in monomer-swollen micelles, so the size and number of micelles (i.e. the nature and concentration of the surfactant) will ultimately determine the number of particles formed and their final size. In other polymerization systems, nucleation may occur from small, dissolved oligomers, in which case the micelles present solubilize unreacted monomer and function as reservoirs to feed the growing polymer particles. The surfactant will also play a major role in the stability of the system. In suspension polymerization, where nucleation and particle growth definitely occur in an emulsified monomer droplet, the final particle size will depend on the size of the initial monomer drops and therefore the characteristics of the surfactant.

In dispersion processes, a new solid–liquid interface is formed, leading to an increase in the potential energy of the system. One role of the surfactant in such processes is to reduce the interfacial energy at the S/L interface, facilitating the formation of new interface and retarding the

aggregation of already formed particles. In porous solids, the surfactant may assist in the dispersion process by improving the wetting of the channels by the liquid, thereby accelerating breakup. Additional roles related to the weakening of solid structure due to adsorption at crystal defects have also been suggested.

The role of surfactants in stabilizing solid suspensions is, again, one of great academic and technological importance. Because of the vast literature available concerning the fundamental and practical aspects of the subject, its pursuit will be left to the interested reader. Suffice it to say that the nature of the surfactant to be used – its adsorption properties, electrical charge characteristics, rheological properties in solution, etc. – should always be considered early in preliminary formulation processes.

13

Special Topics in Surfactant Applications

This chapter is intended to introduce in a little more detail a few important special topics involving areas in which surfactants play an important role. Although “more detail” is the intended purpose, the discussion for each area addressed is extremely broad, and the “details” are far too numerous to reproduce in a single chapter or even a full book or monograph. Each topic is the subject of a large number of books and monographs, not to mention scientific journal publications. The details, presented, therefore, will be very basic, but hopefully sufficiently enlightening as to provide a small window into these interesting and important areas of science and technology.

13.1 Surfactants in Foods

The various interfacial interactions already described in previous chapters are ubiquitous components of food systems. The actions of surfactants are of importance in every stage of food preparation, from the initial preparation of the food in question to determining the physical and organoleptic characteristics of the final product, and its ultimate shelf life in the case of commercial products.

The interfaces of special importance in foods are obvious: liquid–liquid or emulsions, liquid–air or foams, and liquid–solid in the case of dispersions. One or two less recognizable areas of importance, such as crystallization modifiers or inhibitors, will also be mentioned. Controlling the physical characteristics of those interfaces is very important to the quality of the product during preparation, both in terms of its “fresh” state, right out of the oven, so to speak, and the lifetime of the product in terms of how long it will maintain those desired taste and mouthfeel qualities over time. Those initial qualities and their duration during storage and shipping are, as often as not, achieved by including surfactants as emulsifiers, foaming agents, staling inhibitors, etc., along with the normally recognized ingredients for “traditionally” prepared examples. Home cooking “like mother used to make” is great, but such traditional preparations usually do not fare too well when the product is packaged, stored, and shipped days, weeks and often months after they are prepared. While traditional ingredients such as egg whites and yolks have been used as emulsifiers and foaming agents for centuries, sometimes they just cannot maintain the desired product characteristics in the context of the mass-produced, long-distance shipping, and extended shelf storage of the modern world.

Technically, the term “emulsifier” is usually applied to a subgroup of the general surfactant family based on the physical function it is present to fulfill. In food-related applications, however,

the term “emulsifier” is commonly used for all surface-active materials regardless of the actual function involved. With label reading so emphasized in our modern consumer world, especially as related to the things we eat, “surfactant” often carries with it a more “processed” or “chemical” connotation that may not sit well with the less informed consumer, while “emulsifier” has a softer, more friendly sound to most people.

Food products, especially those in the areas of baked good, sauces and puddings, many dairy-based products, confectionary products, and many more, exist because of interactions, sometimes very complex in nature, among the various distinctly different ingredients, both physically and chemically. It is those differences and the sometimes naturally unfavorable interactions they have that make the use of emulsifiers, foaming agents, etc., so important to modern food technology.

13.1.1 The Legal Status of Surfactants in Food Products

It is not surprising that surfactants used as food additives undergo a great deal of scrutiny before they are allowed to be added to the foods we eat. Luckily, most food-grade surfactants or emulsifiers have chemical structures that are closely related to natural substances that are found in the human body or come from natural plant or animal sources that are generally recognized as very unlikely to be a threat to human health. For that reason, many are labeled GRAS or generally recognized as safe, while others undergo various testing regimens to assure that they do not produce undesirable or dangerous side effects in animals or show any tendency toward being mutagenic. In many cases, even if no specific red flags appear in those tests, some materials still receive approval, but with limitations on how much can be added in a given situation. Others may receive a nebulous limit known as “best manufacturing practice,” which essentially means use what you need but no more.

Just about every country has its own system and organization to regulate additives such as surfactants, although the majority usually rely on the European Union (EU) and/or the US Food and Drug Administration (FDA) rules and limitations. In the EU system each surfactant or family is assigned an “E” number, which identifies the chemical nature of the material and its applications in foods. The US system is somewhat more complicated in that, in many cases, the materials receives a different designation depending on the specific application, essentially all beginning with “21 CFR” For example, glyceryl monostearate (GMS or monostearin) has the FDA designations 21 CFR: MISC, GRAS/FS, GMP, 184.1324; <2% of product, macaroni products – 139.110; <3% of product, noodle products – 139.150. Obviously, for a product with many uses, things can get a little complicated. Table 13.1 is a list of a few of the most important surfactants used in foods along with its “E” number. The FDA designations are not given for the sake of simplicity. The numbers provided are examples for the surfactants most commonly used in foods and all are listed as “emulsifiers” even though they may have many other roles to play in the complex world of food science and technology. Complete listings of all food additives having E numbers are readily available on the Internet.

13.1.2 Typical Food Emulsifier Sources

Given the large number of surfactants available today, relatively few have been approved for use in food products. This section will present some information about the most widely used emulsifier types and their chemical characteristics and some aspects of their surface activity. Since these materials are usually derived by the direct modification of natural raw materials such as fats and oils, the finished products will reflect pretty much the fatty acid composition of the original raw

Table 13.1 European Union “E” designations of some important surfactants employed as food additives.

Surfactant	E number	Use
Polyoxyethylene (40) stearate	431	Emulsifier
Polyoxyethylene (20) sorbitan monostearate Tween 60 or Polysorbate 60	435	Emulsifier
Mono- and diglycerides of fatty acids	471	Emulsifier
Acetic acid esters of mono- and diglycerides of fatty acids	472a	Emulsifier
Lactic acid esters of mono- and diglycerides of fatty acids	472b	Emulsifier
Mono- and diacetyl tartaric acid esters of mono- and diglycerides of fatty acids	472e	Emulsifier
Succinylated monoglycerides	472g	Emulsifier
Sucrose esters of fatty acids	473	Emulsifier
Polyglycerol esters of fatty acids	474	Emulsifier
Polyglycerol polyricinoleate	476	Emulsifier
Propane-1,2-diol esters of fatty acids	477	Emulsifier
Sodium stearyl-2-lactylate	481	Emulsifier
Calcium stearyl-2-lactylate	482	Emulsifier
Sodium stearyl fumarate	485	Emulsifier
Sodium laurylsulphate	487	Emulsifier
Sorbitan monostearate (Span 60)	491	Emulsifier
Sorbitan tristearate (Span 65)	492	Emulsifier
Sorbitan monooleate (Span 80)	494	Emulsifier
Sorbitan trioleate (Span 85)	496	Emulsifier

material. That is, they will not be “pure” chemical species, but rather mixtures of a related family of chemical structures. That implies that there may be some differences in composition of the same product derived from different fats and oils. For example, a glycerol monostearate (GMS) based on palm oil will not have the same relative amounts of palmitic (C_{16}) and stearic (C_{18}) acid chains as one prepared using a hydrogenated soybean oil. In most applications that difference will not be likely to result in a significant difference in the utility of the materials, but that may not always be the case. As an example, a GMS made from hydrogenated tallow (beef or mutton fat) has a nominal composition of about 3% C_{14} , 28% C_{16} , 68% C_{18} , and 1% C_{20} fatty acids, reflecting the fatty acid content of the raw material. One prepared using hydrogenated soybean oil, on the other hand, will have a higher content of C_{18} and less C_{16} acid.

While GMS is prepared by rather simple, straightforward esterification or transesterification reactions, other emulsifiers are prepared by more complex condensation, transesterification, and polymerization reactions at high temperatures. Sorbitan monostearate, for example, is made by heating sorbitol and stearic acid together in the presence of a catalyst. The sorbitol cyclizes by removal of a molecule of water to produce a mixture of sorbitan and isosorbides, which then react with stearic acid and other acids present in the raw material mix to produce esters. Therefore, the reaction product mix contains sorbitan esters with the various acids present as well as esters of the isosorbides formed. Di- and triesters are also produced in small quantities. Strict control of reaction conditions makes it possible to produce consistent, reproducible mixtures of the reaction products, but chemical “purity” is never a consideration. Sorbitan tristearate is made by a very

similar reaction, but with a higher stearic acid/sorbitol ratio in the starting mix. Most other food emulsifiers based on natural fatty acid mixtures and polyhydric alcohols will also be mixtures, so when a chemical structure is shown, it is meant to represent the desired material. The reality is something else.

Glycerol monostearate is the major player in the world market for food emulsifiers because of its wide range of direct applications. It is also an important precursor to a variety of additional emulsifiers derived from it by further esterification. It is estimated that GMS represents roughly 75% of total food emulsifier production. The next section will present more information on GMS and emulsifiers derived from it as well as other frequently used materials.

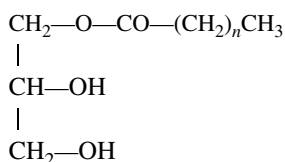
13.1.3 Chemical Structures of Some Important Food Emulsifiers

An in-depth discussion of the science and art of emulsifier use in foods obviously goes far beyond anything presented here. Beyond the “simple” surfactant species discussed, the compositions of foods include a number of non-surfactant species that are naturally present in the basic ingredients, but historically played a primary role in the preparation of traditional foods, both “home-made” and commercial. The most important of those natural ingredients is the proteins and carbohydrates. Although some mention is made of their actions and importance in the production of foods, they will not be discussed in detail. Nominal chemical structures of the most important food emulsifiers are shown in Figure 13.1.

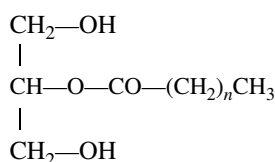
13.1.3.1 Monoglycerides

More than 85 million kg of monoglycerides are used annually in the United States in food products, accounting for approximately 70% of all food emulsifier use. The nominal chemical structure of the principal monoglyceride used in baking, glycerol-1-monostearate, is shown in Figure 13.1a. The same material is also commonly referred to as 1-monoglyceride, 1-monostearin, or α -monoglyceride, among other names, or just GMS. If the stearate unit is bonded at the middle

(1) Acyl glycerides

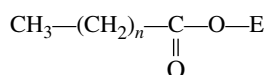


(a) 1- or α -Acyl monoglyceride



(b) 2- or β -Acyl monoglyceride

(2) Esters of long-chain (C_{12} — C_{18}) fatty acids



where E may be a hydroxy carboxylic acid, a polyol such as sorbitan, a polyether such as polyethylene oxide, etc., as illustrated later

Figure 13.1 Nominal chemical structures of important food emulsifiers.

or 2-position on the glycerol, the compound is glycerol-2-monostearate, 2-monostearin, or β -monostearin (Figure 13.1b). Both isomers are equally active in some applications, as discussed below, where the mechanism for that action is through the hydrophobic stearate chain, but the 2-isomer is not as effective in other roles. Manufacturers of GMS usually specify their product according to the α -monoglyceride content. Since in some applications of monoglycerides there is a difference between the activities of the α - and β -isomers, so as a practical matter, the reporting of the amount of α -monoglyceride is logical. The α -isomer usually represents >90% of the total product with the β -isomer and small amounts of free glycerol, free fatty acid making up the rest.

The fatty acid composition of a monoglyceride will always reflect that of the triglyceride fat used as the raw material. Commercial GMS may contain as little as 65% stearate if prepared from fully hydrogenated lard or as much as 87% stearate if prepared from fully hydrogenated soybean oil. The remaining fatty acid is palmitic, although small amounts of oleic and/or elaidic acids may be present if the hydrogenation process is not taken to produce an iodine value (a reflection of the amount of unsaturated fatty acids present) of 0. The typical commercial GMS has an iodine value of about five.

13.1.3.2 Derivatives of Monoglycerides

The common derivatives of monoglycerides shown in Figures 13.2 and 13.3 are of two types: (i) dough strengtheners like succinyl monoglyceride (SMG), ethoxylated monoglycerides (EMG), and diacetyl tartaric acid esters of monoglycerides (DATEM) and (ii) α -tending emulsifiers, such as acetylated monoglyceride (AcMG) (Figure 13.3a), lactylated monoglyceride (LacMG) (Figure 13.3b), and propylene glycol monostearate (PGMS) (Figure 13.3c). Propylene glycol monoesters are not, of course, derivatives of monoglycerides, but the difference is chemically minor in terms of their possible substitution pattern on the available hydroxyl groups. The primary hydroxy or 1-hydroxyl is chemically more reactive than the secondary or 2-hydroxyl position. Thus, acetylation gives mainly 3-acetyl-1-monoglyceride, but there is also a certain amount of

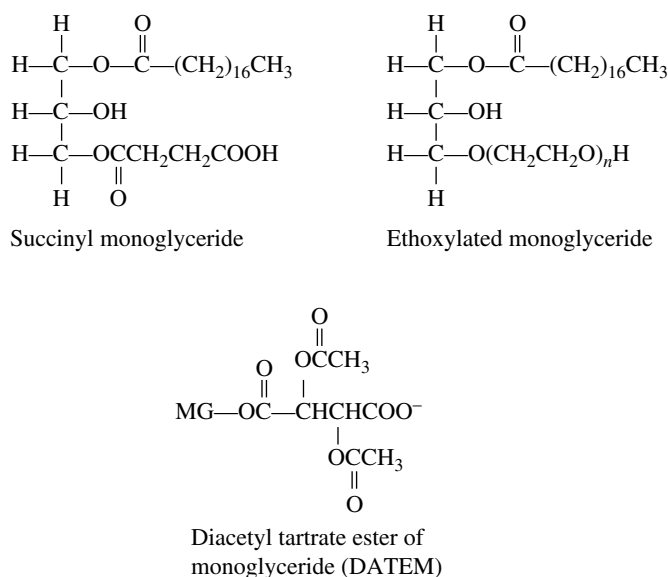


Figure 13.2 Derivatives of monoglycerides classed as “dough strengtheners.”

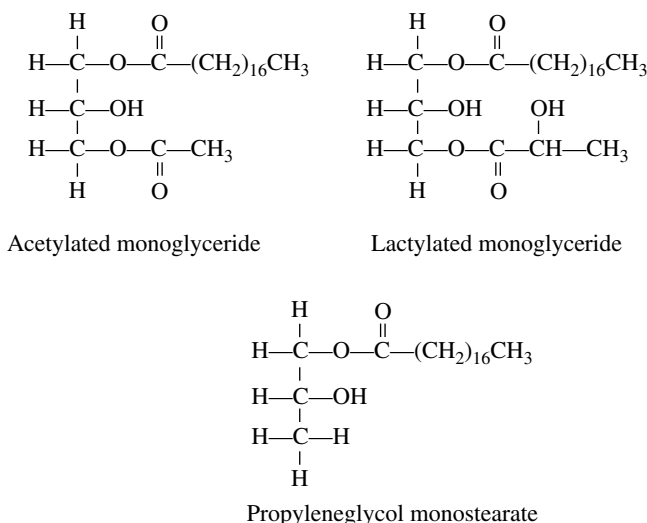


Figure 13.3 Monoglyceride derivatives classified primarily as α -tending emulsifiers.

2-acetyl-1-monoglyceride plus 1-acetyl-2-monoglyceride. In addition, any diglyceride present can also be acetylated.

Succinylated monoglyceride is made by reacting succinic anhydride with monoglyceride. The reaction is fairly straightforward. The various positional isomers mentioned for AcMG can also be found in SMG. DATEM is produced in two steps. First, tartaric acid is reacted with acetic anhydride, acetylating the two hydroxy groups and converting the tartaric acid into the anhydride. This is then reacted with monoglyceride. The major product is diacetyl tartaric acid ester of monoglyceride with the structure shown in Figure 13.2c. Other closely related compounds are present, including di- (diacetyl tartaric acid) ester of monoglyceride, mono- (diacetyl tartaric acid) ester of diglyceride, and mono- (diacetyl tartaric acid) mono acetyl ester of monoglyceride. The ratios of these four components in a given DATEM preparation depend mainly on the content of diacetyl tartaric acid anhydride and the type of monoglyceride used in the reaction. The functionality of the emulsifier depends to a large extent on its composition, so it is necessary to maintain a close control over raw material specifications in order to ensure that performance remains consistent from batch to batch. Important indicator properties for quality control are the saponification value and acid value.

The structure of EMG (Figure 13.2a) is even more random. Monoglyceride is treated with ethylene oxide (EO) gas under pressure at high temperature in the presence of an alkaline catalyst. The EO polymerizes into a polyether (POE) and also forms ether bonds with the free hydroxyl groups of the monoglyceride. The average length of the POE chain is about 20 units ($n = 20$ in Figure 13.2a). Both the 2- (β) and 3- (α) positions of the monoglyceride may react, although the 3- (α) position is more chemically reactive and is more likely to be derivatized. The exact distribution of POE chain lengths and their distribution between α and β positions are functions of reaction conditions such as type and concentration of the catalyst employed, the EO gas pressure, the reaction temperature, the agitation, and the reaction time.

The second group of monoglyceride derivatives mentioned, the α -tending emulsifiers, are used mainly in the baking industry in the production of cakes. These emulsifiers are dissolved in the fat or shortening phase of the cake formulation, where they aid in the emulsification of the shortening in the water phase and also aid in the incorporation of air into the fat phase. The particular property

of these emulsifiers that makes them valuable in liquid shortening cakes is that they form a solid film at the water–oil interface that stabilizes the emulsion; but more importantly, it prevents the lipid phase from destabilizing the protein-stabilized foam during cake batter mixing.

The manufacture of AcMG and PGME involves straightforward organic chemistry. Treatment of monoglyceride with acetic anhydride results in the acetylated product, with the various kinds of possible isomers listed above. PGME can be made either by direct esterification of propylene glycol with fatty acids or by the interesterification of fat triglycerides with propylene glycol. The direct esterification product typically contains about 55–60% monoester, and the remainder is diester. Although a product containing >90% monoester can be made by molecular distillation, the extra cost of this process is not warranted for most commercial cake mix production uses. The interesterified product mixture is more complex, containing not only mono- and diesters of propylene glycol but also about 10–15% monoglyceride and a small the amount of diglyceride. As with DATEM, because such a wide range of product compositions are possible from different manufacturing processes, it is necessary to have stringent raw material specifications for this ingredient.

Lactic acid esters of monoglyceride are usually made by reacting lactic acid with a distilled monoglyceride. The complication in this seemingly simple process is that the lactic acid also contains a reactive hydroxyl group and during the high temperature reaction, the fatty acid group may migrate. For example, if lactic acid is heated with GMS, the main initial product is 3-lactoyl-1-stearoyl glycerol. However, during the reaction, some portion of the stearic acid may migrate to the lactic acid hydroxyl group producing glyceryl 3-(stearoyl)-1-lactylate. In addition, lactic acid can polymerize to form lactoyl lactic esters and lactoyl dimers and trimers may also be produced. Therefore, the reaction product mixture from reacting lactic acid with monoglyceride may have as many as 10 identifiable molecular species. Production parameters therefore must be very tightly controlled to obtain a product with consistent functionalities. By now, just the simple act of trying to remember the names of the many possible products of these reactions has produced a headache as a reaction by-product.

13.1.3.3 Derivatives of Sorbitol

When the sugar alcohol sorbitol is heated with stearic acid in the presence of a catalyst, two reactions occur: sorbitol cyclizes to form the five-membered sorbitan ring, and the remaining primary hydroxyl group is esterified by the acid. The resulting sorbitan monostearate, also commonly known as Span 60 (Figure 13.4a), is oil soluble and has a rather low hydrophile–lipophile balance

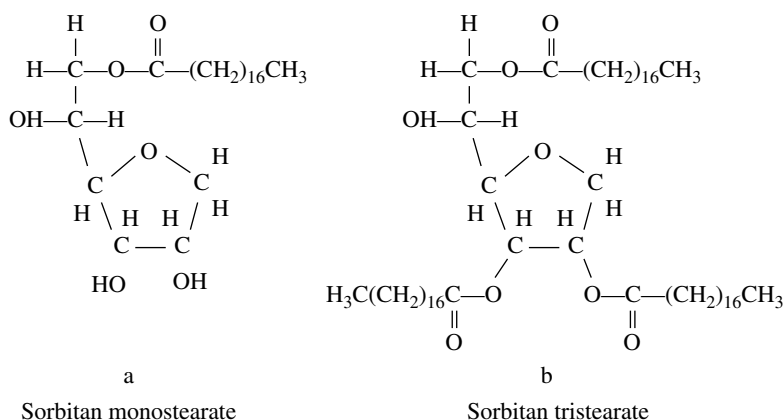
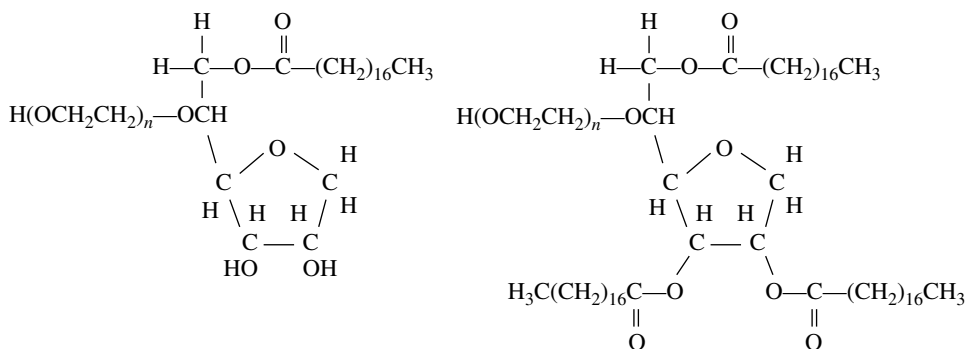


Figure 13.4 Structures of sorbitan esters.



Ethoxylated sorbitans: monoethoxylated Polysorbate 60 (also known as Tween 60) and triethoxylated Polysorbate 65 (or Tween 65). The degrees of ethoxy substitution are approximate values

Figure 13.5 Basic structure of polyhydric emulsifier molecules.

value. The triester (Span 65) (Figure 13.4b) is even more hydrophobic. Both of the sorbitan esters illustrated, as well as others esterified with other fatty acids, can be reacted with EO to obtain polyoxyethylene (POE) derivatives shown in Figure 13.5. The monostearate derivative is commonly known as Polysorbate 60 or Tween 60, the triester as Polysorbate 65 (Tween 65), and the monooleate as Polysorbate 80 (Tween 80). The general information given for the ethoxylation to produce EMG regarding the links and location of the POE chains applies to the polysorbate compounds as well. The average number of oxyethylene monomers is 20, and in the case of the monoesters, the chains may be located on more than one hydroxy group of the sorbitan ring. In the case of the triester, of course, only one hydroxyl group is available for derivatization.

Sorbitan monostearate is a good emulsifier for use in making cake and pastry icings producing superior aeration, gloss, and stability characteristics. It is also used as part of the emulsifier system in whipped toppings and in coffee whiteners. The POE derivatives have found wide acceptance in general with Polysorbate 60 being the most widely used of the group. At a level of 0.25% based on the weight of flour in the recipe, the ability of Polysorbate 60 to strengthen doughs against mechanical shock is greater than that of SMG and about equal to that of EMG and sodium stearoyl lactylate (SSL). Polysorbate 60 has also been used in fluid oil shortening systems, usually in combination with GMS and PGMS.

One of the great advantages provided by the chemistry of the sorbitan esters, both the simple esters and the ethoxylated materials, is that the HLB values can be readily adjusted over a range of about 4–17. They also make it relatively easy to produce a tailor-made HLB value by using the proper combination of two members of the family.

13.1.3.4 Polyhydric Emulsifiers

Polyhydric alcohols are those that have several free hydroxyl groups potentially available for esterification during the manufacturing process (Figure 13.5). Organic chemistry being how it is, of course, all available —OH groups may not be equally reactive under a given set of reaction conditions due to chemical reactivity questions (primary versus secondary hydroxyl groups) or due to steric crowding around different positions. As a result, the exact product composition may vary different reaction conditions.

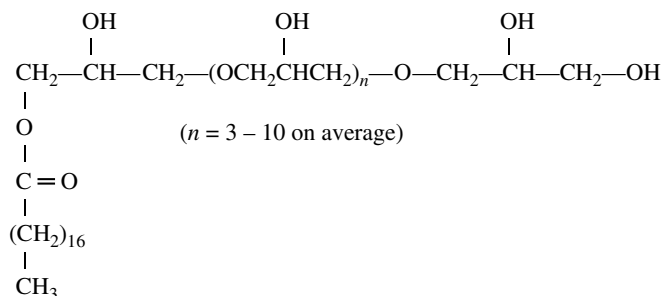


Figure 13.6 Typical structure of polyglycerol esters.

13.1.3.5 Polyglycerol Esters

Polyglycerol esters (Figure 13.6) have a variety of applications in the food industry. The polyglycerol chain is produced by heating glycerol in the presence of an alkaline catalyst, and ether linkages are formed between the primary hydroxyl groups of glycerol. In the structure shown in Figure 13.6, n may take any value, but for food emulsifiers, the most common values are $n = 3, 6, 8,$ and 10 . In all cases, the numbers represent average values in commercial preparations. The polyglycerol backbone is subsequently esterified to varying extents by direct reaction with a fatty acid or by interesterification with a triglyceride fat. As usual, the number of acid groups esterified to a polyglycerol molecule will vary around some average value determined by the conditions of the reaction. Also, as seen before, good control of the feedstock and reaction conditions is vital for producing materials with approximately the same properties from batch to batch.

The HLB values of the polyglycerol esters depend on the length of the polyglycerol chain and the degree of esterification. For example, decaglycerol monostearate has an HLB of 14.5, while triglycerol tristearate has a value of 3.6. As with the sorbitan family of emulsifiers, with appropriate blending, a good range of HLB values can be produced with polyglycerol esters.

13.1.3.6 Sucrose Esters

The common table sugar sucrose has eight free hydroxyl groups, which are all potential sites for esterification with fatty acid. Compounds containing six or more fatty acids per sucrose molecule are not emulsifiers but are sold as noncaloric fat substitutes. Those materials act like triglyceride fats and have no surfactant properties. Compounds having from 1–3 fatty acid esters (Figure 13.7) do act as emulsifiers and are approved for food use in that application. The manufacturing process

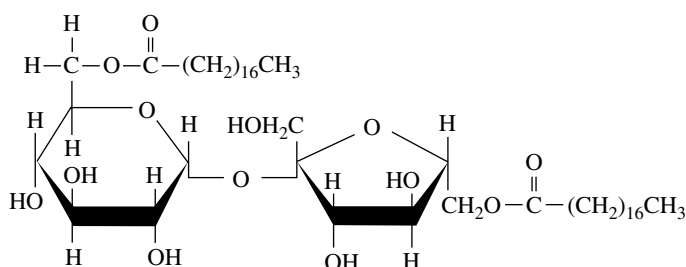


Figure 13.7 Sucrose ester structures.

for sucrose esters is more complex than that for most food emulsifiers, which helps explain their higher overall cost relative to most of the material previously discussed, although that cost is justified in some applications.

As usual, the degree of esterification is controlled by the reaction conditions, especially the ratio of sucrose to the methyl ester of the fatty acid being esterified, and the final product will be a mixture of the various possible esters. Also, as expected, the HLB value of a product decreases as the degree of esterification increases for a given fatty acid and increases as the length of the fatty acid chain decreases from C₁₈ to C₁₂ or below.

13.1.3.7 Anionic Food Emulsifiers

The discussion up to now has been dedicated primarily to nonionic emulsifiers and a few anionic materials in the special context of the bread baking industry. However, other anionic emulsifiers have found good homes in many areas of food technology, and, as pointed out, especially in the baking industry. In addition to SMG and DATEM, SSL, sodium stearoyl fumarate, and sodium dodecyl sulfate (Figure 13.8) have been tried as dough strengtheners. SSL is currently the most widely used in the United States, although its use is limited or prohibited in some European countries. Sodium stearyl fumarate, which from its structure might be expected to function similarly to SSL, did not seem to produce enough of the desired effect for the application and never became popular, although it still has FDA approval for some applications. Sodium lauryl sulfate, the commercial analogue to pure sodium dodecyl sulfate, was also tried, but never really implemented as a competitor to SSL for baking applications. However, it is used as a whipping agent when combined with egg whites.

Lactic acid, with both a hydroxyl group and a carboxylic acid group on the same molecule, readily forms an ester with itself. In commercial concentrated solutions, almost all of the acid is present as the polylactic acid polymer. To get free acid it is necessary to dilute the acid significantly with water and heat or reflux it for a time. When stearic acid is heated with polylactic acid under the proper reaction conditions and then partially neutralized with sodium hydroxide, a product with the nominal formula shown in Figure 13.8 is obtained. The monomeric lactic acid shown represents that predominate product, but the dimeric lactic acid is also present in significant quantity

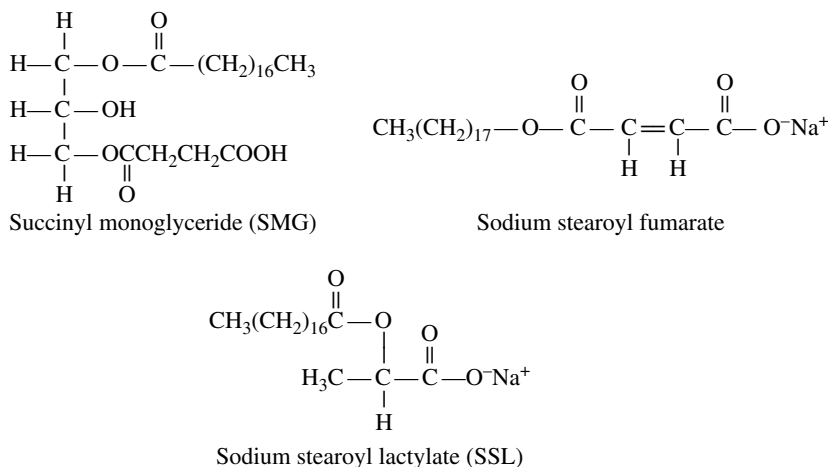


Figure 13.8 Dough strengthening emulsifiers having hydroxy carboxylic acid units.

as well as smaller amounts of the trimer and tetramer acids. As with all compounds based on commercial stearic acid derived from hydrogenated fats, some percentage of the fatty acid is palmitic, and small amounts of myristic and arachidic (C_{20}) acids are also present. The partially neutralized SSL is slightly soluble, but readily dispersible in water. The molecule can also be prepared as the calcium salt and generally functions well as a dough strengthener, depending on the conditions of use, but it is insoluble in water and more difficult to disperse. When used as a stabilizer for hydrated GMS, however, only the sodium salt is effective since in that function the SSL molecule must be ionized in the water layer.

13.1.3.8 Lecithin

Lecithin is a “natural” surfactant mixture prepared as a by-product of the processing of crude soybean oil. Although it is routinely referred to as a single product, it is, in fact, a mixture of three primary chemical compounds mixed with smaller amounts of additional materials. It is the major component of the “gum” that is removed during the beginning step of oil refining. The crude gum is treated and purified to produce various commercial lecithin products that are available today. Crude soybean oil contains about 2% lecithin, while crude corn and cottonseed oils contain about 1%. Because smaller amounts of these oils are processed in the United States compared with soy oil, the amount of gum obtained is usually too small for economical processing for human food uses. Instead, it is added back to animal feed formulations where it provides a valuable source of energy. Egg yolk contains about 20% phospholipid, which accounts for its excellent emulsifying functionality, for example, in mayonnaise. However, lecithin isolated from egg yolk is too expensive to be used for commercial food manufacture.

In the purification process for soy lecithin, the gum is dehydrated to remove water added during degumming, and then insoluble fines (small particles) are removed by filtration. The crude material is brown to dark brown depending on the amount of heat applied during the processing and contains some pigments extracted from the original soybean. It is then bleached to attain a more acceptable light brown color. Treatment with up to 1.5% hydrogen peroxide results of a product known as single bleached lecithin, and addition of benzoyl peroxide up 0.5% yields double bleached lecithin.

The phospholipids in lecithin are insoluble in acetone, and the phospholipid content of lecithin is specified as acetone-insoluble (AI) materials. The standard commercial lecithin has a minimum AI content of 65%. Crude bleached lecithin is quite viscous, but the addition of vegetable oil fluidizes it, and commercial fluid lecithin products are standardized to have a viscosity of between 7 500 and 10 000 centipoises at 25 °C. A fully de-oiled lecithin, a granular, free-flowing powder product with a typical AI content of 95–98%, is also available.

The structures of the main surface-active components of lecithin are shown in Figure 13.9. The phosphatidyl group is a phosphate ester of a diglyceride. The fatty acid composition of the diglyceride is similar to that of the basic soybean oil, so a number of different fatty acids are found, not just those illustrated. The three main surface-active components are usually present in approximately equal amounts. Phosphatidylethanolamine (PE) and phosphatidylcholine (PC) are amphoteric surfactants, while phosphatidylinositol (PI) is nonionic. Other surface-active species are also present in smaller amounts, including lysophosphatides and glycolipids. The lysophosphatides are similar to the main components above, but with one fatty acid removed from the molecule, making them more hydrophilic. The glycolipids contain a sugar residue, either galactose or di-galactose, attached to the free hydroxyl group of a diglyceride.

The HLB values of the three principal components vary: PC has a high HLB, PE an intermediate value, and PI a low value. The HLB of the natural blend is 9–10, and emulsifier mixtures with

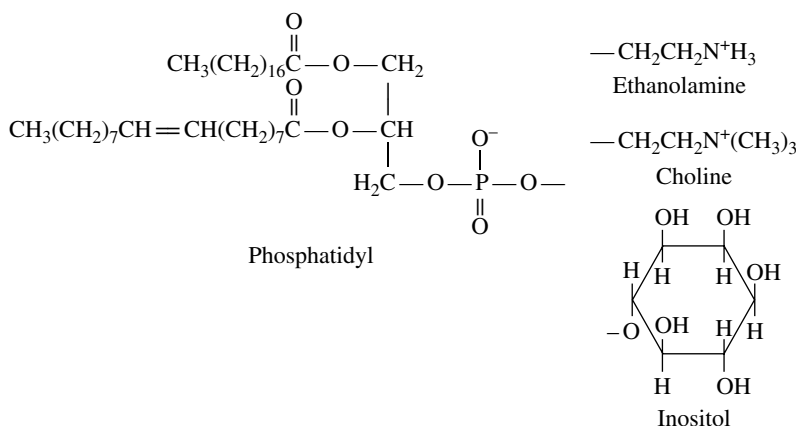


Figure 13.9 Structures of lecithin components.

values in this range tend to form both oil-in-water (O/W) and water-in-oil (W/O) emulsions, although neither type is particularly stable with lecithin alone. However, emulsifiers with intermediate HLB values like lecithin tend to be excellent wetting agents, and this is an important application for the product.

The emulsifying properties of lecithin can be improved by ethanol fractionation. PC is soluble in ethanol, PI has low solubility, and PE is only slightly soluble. Adding de-oiled lecithin to ethanol produces two fractions, one soluble and one insoluble. The soluble fraction usually has a phosphatide composition of about 60% PC, 30% PE, and 2% PI plus glycolipids. The insoluble fraction is usually 4% PC, 29% PE, and 55% PI plus glycolipids. The remaining small percentage of both fractions includes oil, free fatty acids, and lysophosphatides. The soluble fraction is most effective in forming and stabilizing O/W emulsions, while the insoluble portion forms and stabilizes W/O emulsions. Products with up to 90% PC can be prepared by preparative chromatography of the ethanol fraction. The method can be used to obtain a material containing 90% PC that has been used to make an egg yolk replacer. The good emulsifying ability of egg yolk lecithin results in part from its HLB arising from its high content of 70% PC and 15% PE in the total phospholipid, plus the presence of effective protein stabilizers. The chromatographic process is currently used by several European companies to produce industrial food-grade emulsifiers with special functionalities. The process of preparative chromatography, however, can be quite expensive, both from an equipment standpoint and a yield standpoint.

13.2 Some Important Functions of Surfactants in Food Products

The importance of surfactants in the success of modern food technology cannot be overemphasized. Whether the ingredients are “natural” materials or a commercially produced “synthetic” compounds, their use in most modern commercial food products is vital to the quality and shelf life of most of what we buy in the supermarket or restaurants. The following sections are brief “snapshot” overviews of some of the important food groups that rely on surfactants to make them viable commercial consumer products. The information will, obviously, not be comprehensive, but should help indicate the importance of the surfactant family of chemical species.

13.2.1 Emulsifiers as Crystal Modifiers in Food

For the industrial application of fats and food emulsifiers, crystal structure and its long-term stability represent important questions and sometimes challenging problems. With fats and some emulsifiers, the problem is one of crystal formation itself. Many applications, whether inherent in the nature of the product or a result of a specific application, require special actions to prevent a thermodynamically driven recrystallization process from changing the characteristics of a product to the extent it becomes undesirable or even unacceptable. For example, salad oils, especially extra virgin olive oil, unless it has been modified in some way, will become cloudy due to crystal formation if stored in the refrigerator or even a cold kitchen. The cloudiness is a result of the nature of the fatty acid content of the triglycerides present in the product and in no way affects the utility of the product when brought back to room temperature. However, taking out a bottle of cloudy oil tends to be surprising and distasteful to the ordinary consumer and can result in unhappy complaints to the seller or manufacturer. The user just does not have the advantage of special knowledge about fats and oils. Other vegetable oils have similar tendencies, especially in cold climates, so that it has become routine for producers to “winterize” their products by cooling them down significantly and then removing the crystallized materials by filtration or centrifugation. In the case of extra virgin olive oil, that is not legally an option in most countries. In addition to being visually unacceptable, crystallization may have more serious effects in emulsified food products such as mayonnaise, salad dressings, and margarine. Crystal formation in those classes of emulsified products can result in the breaking of the emulsion and the separation of the oil and aqueous phases, which would obviously be disastrous.

In most oils subject to clouding, the amount of crystallizable material is usually only 1–2%. However, the winterizing process is seldom completely effective so that in some cases, additional steps may be necessary to prevent the problem. The principal method for that has been the addition of crystal inhibitors. Such inhibitors are usually emulsifiers such as sorbitan monostearate and oxystearin, a partially oxidized mono-diglyceride usually derived from vegetable oils. Other emulsifiers such as polyglycerol esters, polyoxyethylene sorbitan esters, and sucrose esters are also effective.

Triglyceride crystals, like in most materials, grow by the incorporation of additional fat molecules to the surfaces of already formed, but extremely small seed crystals, ultimately leading to the formation of visible crystals. Inhibitors present in the liquid oil will also effectively adsorb on the growing crystal faces. However, those materials are not conformationally identical to the original face, additional triglyceride molecules cannot be added, and the crystals remain small and essentially invisible to the naked eye. When the oil in question warms to a temperature above that leading to crystallization, many if not all the small seed crystals will melt back into the liquid. In effect, the utility of the oil is maintained, or its shelf life is extended.

To be acceptable to most consumers, shortenings and margarines must have a smooth, plastic consistency, which results from bringing about crystallization of the fatty material under conditions that produce what are termed β' crystals. But since that form is not the most thermodynamically stable one, the crystals will transform into the β form, thereby changing the texture to a grainy, non-plastic consistency that may be unacceptable for many applications. That process will be accelerated if the product is improperly stored, such as at a higher than recommended temperature or for a very long time. The fatty acid chains in the β crystals are slightly more compact than in the β' state. The addition of small amounts (1–3%) of an emulsifier such as sorbitan monostearate or triglycerol-1-monostearate can retard recrystallization by incorporating into the small early-forming β crystals and distorting the crystal faces to such an extent that additional free triglyceride will not be added

and further transition to the β form will be prevented or at least inhibited significantly, thereby protecting the shelf lives of the products. In this case, the emulsifier may also be referred to as a “crystal stabilizer” since its action is to stabilize the β' crystals relative to the β form.

Sorbitan tristearate is an even more effective inhibitor of transformations into β crystals and is used extensively in the confectionary industry for the stabilization of dark chocolate coatings. “True” chocolate coatings, that is, those not composed of or containing cocoa butter substitutes (CBS), are prone to the formation of “bloom,” which is seen as the development of white or unsightly light patches on the surface of the product. Those discolorations are a result of the polymorphic recrystallization (β' to β) of solid cocoa butter fats. As in shortenings and margarines, the addition of an effective crystal modifier, whether you call it an inhibitor or stabilizer, will guarantee that the product meets its expected shelf life aims, unless it is “abused” by excessively high temperatures, for example.

Some shortenings and margarines are prepared with the addition of 1-monoglycerides to enhance their ability to incorporate air in the preparation of sponge cakes and similar food products. Unfortunately, 1-monoglycerides tend to increase the speed of the β' to β crystal transformation. An additional amount of a crystallization modifier such as sorbitan tristearate must be added to counteract that tendency.

The story of phase phenomena, including “simple” crystallization, is complex, and an in-depth discussion is well beyond the scope of this work. The concept of mesophases has already been introduced as applied to surfactants in general, and those concepts apply well to food systems and will not be repeated here. However, it should be pointed out that mesophase structures of emulsifiers in food can significantly affect their interactions with other food components such as proteins and starches and therefore the ultimate functionality of the finished product.

Perhaps the most widely studied example is the interaction of long-chain saturated monoglycerides with the helical structure of gelatinized (hydrated) starch. It is well known that the helical structure of a starch molecule can form a complex with the linear hydrocarbon tail of a saturated monoglyceride emulsifier. Emulsifiers such as 1-monoglycerides are widely used as “anti-staling” agents in breads and other bakery products. A stale bread is not one that has deteriorated in a chemical or biological sense, but one in which the soluble starches in the product have “retrograded” or undergone a reversion from their gelatinized form the fresh baked bread to an original crystallized form. That process begins immediately after the bread or other products is removed from the oven and begins to cool. The baked product, if it does not include a component or additive – that hated term in so many quarters – to retard the retrogradation process, may begin to exhibit a “non-fresh” to stale mouthfeel and taste within a day of its preparation. Unless one lives in an area where fresh baked bread is available daily, eating “stale” bread would be a way of life.

Extensive studies have shown that the complex formed between the starch and the emulsifier tail (Figure 13.10) forms most effectively when the emulsifier is present as a lamellar mesophase from which the inclusion of the GMS molecule in the helical structure is greatly facilitated. The same anti-staling effect can be expected from other emulsifiers with long-chain saturated tails such as SSL, DATEM, and polyoxyethylene sorbitan monostearates, among others. These emulsifiers are commonly referred to as “dough strengthening” additives due to the fact that they exhibit other interactions with baking ingredients such as starches and flour proteins that improve the kneading characteristics of the mix, the ability of the resulting dough to form and retain a high degree of fermentation gas retention, more uniform bubble size and distribution, better humidity retention in the finished product, and a number of other product qualities that make commercially baked bread and other products readily available to large markets.

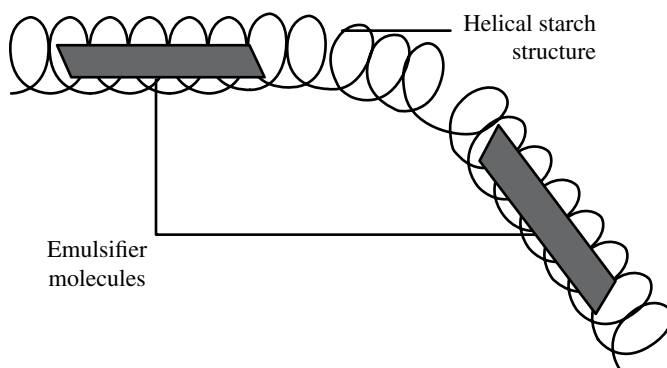


Figure 13.10 Schematic representation of the proposed starch–emulsifier complex.

The interactions of emulsifier mesophases with proteins in foods have not been as extensively detailed as those for starches, but more speculative ideas have been put forward that suggest that significant interactions do occur. The dough strengthening emulsifiers noted above are known to form mesophases in doughs at the water contents and temperatures employed in the bread making process, especially during kneading and proofing, which is a final “rest period” to allow the raw dough to ferment and rise before entering the oven. The dough must have the physical “strength” to accept and maintain the desired volume before entering the oven and resist abuses such as physical bumps, abrupt temperature changes, air currents, and the like. Since the physical strength of the dough and final product comes from the protein gluten, it is easily assumed that the emulsifiers present in most modern industrially baked bread must have some interaction with those proteins. The exact nature of that/those interactions has not been definitively identified.

13.2.2 Bakery Products

Surfactants used in the production of bakery goods are usually referred to as either “emulsifiers,” “anti-staling agents,” or “dough strengtheners.” From a physical chemist’s point of view, the way these terms are used is scientifically inaccurate – almost meaningless. To the industry technician, on the other hand, they mean exactly what they want them to say. They are perfectly descriptive ways of defining their use in baked products. The roles that these materials play at interfaces are explained here, but current bakery terminology is used for the sake of convenience in many places. Strictly speaking, an emulsifier is simply a surfactant that promotes the formation of an emulsion; that is, it facilitates the subdivision of one immiscible phase into drops or particles dispersed in the continuous phase. In bakery terms, this function is most important and the production of batters for cakes, cake doughnuts, waffles, etc.

The term emulsifier is also applied to compounds such as “crumb softeners” that interact with molecules and granules of starch and slow the rate at which they request recrystallize or “retrograde,” thereby contributing to the retention of crumb softness. Surfactants that perform that role act at the solid–liquid interface, not the liquid–liquid interface as it would as an emulsifier.

Dough strengtheners are surfactants that presumably interact with gluten proteins and enhance dough characteristics that bakers refer to as dough strength. In that function the surfactant is acting at a solid–liquid rather than a liquid interface.

All bakery surfactants also aid in the incorporation and subdivision of air into the liquid phase; that is, they promote foam formation. This is important in cake production and in the generation of

fine-grained crumb in bread. Compounds used for this purpose are usually called emulsifiers, although they are actually functioning as foaming agents that function at the gas–liquid interface.

Finally, it should be noted that any given surfactant may function in all the ways listed, even though it is used primarily for one specific function. For example, SSL is used mainly for its dough strengthening effect, but it functions as a true emulsifier, foaming agent, and an agent for maintaining crumb softness and prolonging the shelf life of the finished product.

Again, from the viewpoint of the physical chemist, a bakery dough is a very “messy” system involving many simultaneous interfacial interactions. For a better understanding of those interactions, it may be helpful to isolate each type of interaction for discussion, keeping in mind that ultimately all functions must be considered together to realistically assess the effects of surfactants on bakery goods.

13.2.2.1 Anti-staling Agents

Emulsifiers were first used in bread to extend shelf life, that is, to retard staling maintaining the flavor and mouthfeel of fresh baked bread, the consumer demands for a longer period of time during shipping from the production facility to the store shelf. Monoglycerides are the primary anti-staling additives used today and represent about 1/3 of the emulsifiers used in the baking industry. Staling is a complicated process that involves changes in all of the components of bread, and it is actually a sensory response reflecting the sensation that older breads “taste stale.” A decrease in the “fresh” flavor impact and/or a drier mouthfeel can be sensed by the least discerning consumer and evaluated numerically by professional tasting panels. However, even before a sample is tasted, most consumers and professional tasters can detect staling with a simple squeeze test. Staleness is often equated to the resistance of a bread loaf to manual squeezing. Bakery quality-control laboratories and research groups assess staleness by measuring the resistance of the crumb to compression in one of several available instruments. The evaluations of professional tasting panels correspond surprisingly well with the laboratory results obtained from instruments. The instruments measure what is called the “elastic” or “crumb” modulus, which is its resistance to compression. The tasting panels evaluate the sample based on flavor, mouthfeel, and texture. There is usually a very good linear correlation between the value scores of the panels and the logarithm of the compression modulus.

From extensive research on staling, three important conclusions have been drawn:

- 1) Staling is not related to moisture loss from the bread. A five-day-old bread sample stored under the proper conditions has the same moisture content as a fresh loaf, although it has a drier mouthfeel to a taster.
- 2) Staling is related to the recrystallization or retrogradation of the starch molecules gelatinized during the baking process. Interestingly, it can usually be observed that bread stored in a refrigerator will show retrogradation more rapidly than bread stored at room temperature since the lower temperature favors recrystallization. On the other hand, bread stored in the freezer, when removed and thawed, will generally have almost the same “freshness” feel and taste as it did when frozen. A possible explanation for that phenomenon might be that when frozen the water molecules involved with the gelatinized starch are immobilized, the starch molecules cannot move in a way that allows reconfiguration of the chains to the crystallized configuration.
- 3) Other bread components such as gluten and pentosans (polysaccharides composed of five-membered ring saccharides) may play a role in staling, but the extent and nature of that effect has not been determined as yet.

The chemistry involved in the gelatinization of starch molecules in bread baking is an interesting story, but too long to be told in this context. However, the explanation for how surfactant molecules are involved with the starch is worth a short discussion.

13.2.2.2 Starch–Emulsifier Complexation

Gluten proteins and starch are usually thought of as hydrophilic molecules, readily wetted by water and becoming soluble as their molecular weight decreases. However, they are, in fact, amphiphilic. For example, starch has a large number of hydroxyl groups present in the main structural component α -D-glucopyranoside (Figure 13.11a), which is not, of course, flat, but bent in the classic “chair” configuration. As a result, the hydroxyl groups are oriented to the side of the polymer chain in the plane of the ring while the hydrogen atoms are directed either above or below that plane. Therefore, the perimeter of the chain is hydrophilic and the two “faces” somewhat hydrophobic. The separate rings are bound mostly through α -1,4 acetal bonds, and because of the bond angles, the starch chain tends to form a helix with about 6 rings per turn (Figure 13.11b). The situation is difficult to represent in a two-dimensional drawing, but molecular models suggest that the configuration results in most of the hydrogen atoms pointing toward the center of the helix while the hydroxyl groups tend toward the outer surface. That is, the helix configuration forms something like a hollow tube approximately 0.45 nm in diameter. The hydrophobic character and size of the inner tube are such that a straight-chain hydrocarbon such as stearic acid can fit comfortably into the that space (see Figure 13.10). The hydrophilic nature of the “surface” of the helix also makes it prone to direct interactions with surfactants in the aqueous phase. The exposed hydrophilic portions of the helix are available for hydrogen bonding interactions with appropriate emulsifiers in the solution. Such interactions might help explain the ability of some emulsifiers to slow starch retrogradation or recrystallization in baked products, thereby prolonging their acceptable shelf lives.

Extensive experimental evidence confirms that such starch–alkyl chain complexes are formed rather easily so long as the alkyl chain is “straight” and longer than 12 carbons in length. Three “rules” have evolved related to starch–emulsifier complexes:

- 1) Saturated fatty acid residues with 12–20 carbon atoms as are common in most food emulsifiers make the best complex formers.

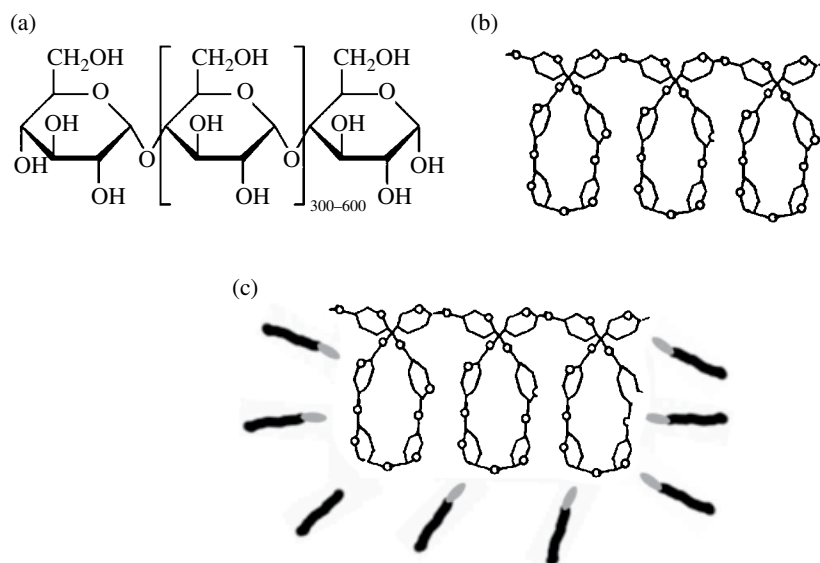


Figure 13.11 Representations of other starch–emulsifier complex configurations (a) the chemical structure of amylose, (b) the amylose helix, and (c) emulsifier molecules associated with the hydrophilic exterior of the starch helix.

- 2) *cis*-Unsaturated fatty acid chains such as oleic residues are very poor complex formers because the bend introduced by the *cis*-double bond makes it very difficult for the chain to fit into the interior of the helix tube.
- 3) *trans*-Unsaturated fatty acids such as elaidic acid, the *trans*-equivalent to oleic acid, do form good complexes since the *trans*-double bond essentially “straightens” the alkyl chain so that it again fits into the internal tube of the helix.

Many years of research and experience have shown that there is a direct correlation between the ability of a monoglyceride-based emulsifier with a straight-chain hydrophobic group to form complexes with starch and its effectiveness at retarding the staling of breads and other baked products. For example, studies of staling for breads baked with different, but closely related, emulsifiers, plus a control, of course, showed that staling in breads baked with 1-monopalmitin and 1-monostearin was retarded by two days, while breads baked with 1-monoolein and 1-monolinolein became stale at the same rate as the control baked without emulsifier. It was also found in the studies that for maximum effectiveness, the saturated monoglyceride should be added to the dough mix as the lamellar mesophase (Chapter 7). That result could also explain the observation that anti-staling results are improved when two (or more) emulsifiers such as GMS and SSL or GMS and Polysorbate 60 are employed together. Such synergism between surfactants is not at all uncommon. In fact, a good “rule of thumb” for many surfactant applications is that smaller amounts of two (or more) surfactants will often produce a better result than a larger amount of a single material.

In summary, then, the question of bread staling and the effects of emulsifiers on it can be stated as:

- 1) Staling or crumb firmness during storage results primarily, although not necessarily exclusively, from the retrogradation or recrystallization of gelatinized amylopectin in the starch.
- 2) Emulsifiers with long, straight-chain hydrophobic groups form complexes with the gelatinized amylopectin that retards the reversion of the chains to the crystalline state.
- 3) Emulsifiers also form complexes with the solubilized amylose chains and may also retard its participation in the re-formation of the solid intergranular starch matrix of the native starch.

13.2.2.3 Dough Strengtheners

The effect known in the baking industry as “dough strengthening” is related to the physical state of primarily the gluten proteins in the flour at the time of dough mixing, “proofing” or dough fermentations to produce the gases needed for dough volume, and baking. The reasons why some food emulsifiers act as dough strengtheners while others do not reflect the interesting and somewhat complex interactions among the emulsifiers, the gluten proteins, and other components in the system.

Some of the amino acid side chains on proteins are hydrophobic and are usually buried in the interior of the folded protein molecule, but they become exposed if the protein is unfolded or denatured. It is common that even in the “natural” protein configuration, some of those hydrophobic regions are partially exposed. Such exposed regions are sometimes referred to as “hydrophobic patches” on the protein surface (Figure 13.12). The hydrophobic tails of surfactants can interact with these hydrophobic patches and can contribute to the unfolding or denaturation of the protein, further exposing hydrophobic regions of the protein and further binding of surfactant. Gluten proteins contain about 40% hydrophobic amino acids, and it can interact strongly with lipids. In a dough mixture, more than half the native lipids plus any added surfactant such as SSL are bound to the proteins and can be extracted from the dough. That is, the protein has been denatured and can be solubilized in water. Some of the “unusual” properties of gluten proteins from wheat flour can be explained based on their significant content of hydrophobic regions in the molecules relative to the proteins present in other flour from ground seed grains.

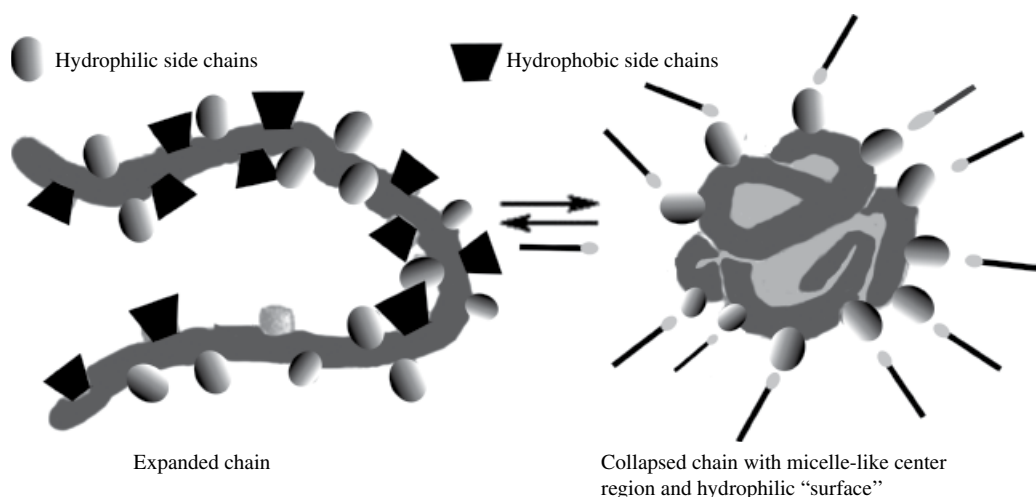


Figure 13.12 Emulsifier interactions with protein structures in solution.

When wheat flour–water dough is acidified, some of the gluten protein is solubilized, probably due to the formation of new electrical charges along the protein chains. At approximately pH 6, the gluten chains have approximately equal numbers of cationic (lysine, arginine, and histidine) and anionic (glutamic and aspartic) amino acids, so there is no significant ionic impulse for water solubility. As the pH is lowered, the anionic acids are protonated (lose their charge), and the protein molecule becomes positively charged. At pH 6, the protein molecules can take configurations that allow a maximum of interactions among the hydrophobic regions, and the molecule can “curl up” into a cozy ball. At pH 3, the net positive charge introduces a net internal repulsion, opening up the configuration (denaturing) of the chains and permitting solubilization. The situation is similar to the stabilization of an emulsion by adsorbed charged surfactant molecules (Chapter 10), pushing the particles apart and preventing contact necessary for drop coalescence. The presence of salt collapses the protective electrical double layer and drop coalescence and protein collapse can result. Most dough strengthening surfactants like SSL are anionic, and adsorbing onto the hydrophobic regions of the proteins counteracts or neutralizes the net positive charge at low pH and facilitates the collapse and aggregation of the gluten. Salt and SSL have similar effects on the dough, although for different reasons. The end result is that both can lead to a collapse of the gluten protein chains, which results in a stronger dough structure. Although a high concentration of most ionic surfactants can solubilize gluten proteins, nonionic and amphoteric species such as Spans, Polysorbates (Tweens), lecithin, etc. have limited solubilizing effects and are not useful as dough strengthening agents.

The questions of the mechanisms of action of emulsifiers in the complex universe of baking go well beyond the points outlined above. However, it is hoped that the interested reader will make a deeper incursion into that universe.

13.2.2.4 Aerating Agents

Most bakery products require the incorporation of air (or gases produced during fermentation) during their preparation stages. The amount and degree of subdivision of the incorporated gas has a significant impact on the physical nature and consumer desirability of the finished product. In a mixed batter, for example, the air bubbles introduced during the mixing serve as nuclei for the gases produced by the fermentation or chemical leavening agents present in the mix. If the air is present as large bubbles, the resulting crumb will be coarse, while more numerous small air bubbles will

produce a smoother, fine-grained crumb. The presence of emulsifiers, whether natural as from eggs or added, will aid in the incorporation of air and produce smaller and more numerous bubbles.

The successful production of good-quality, consumer-acceptable products requires the dispersal of air throughout the batter and the retention of the bubbles until the starch has gelatinized and the structure of the cake or other product has set. In traditional cake baking, a three-stage process was required: (i) first, sugar and shortening or other solid lipid material were vigorously beaten or “creamed” together to incorporate air; (ii) eggs were blended into the aerated material; and (iii) the flour, milk or other liquid plus flavors, colorants, and other ingredients were gently (to avoid destroying the aerated structure) blended in to produce the final batter. That process is great for homemade cakes but is economically impractical for commercial mass production of quality products. For such products, it was necessary to develop a different approach – a relatively rapid one-step process.

One approach was to use a liquid vegetable oil in place of a plastic (solid) shortening for the aeration of the batter. The liquid oil was easier to mix than the shortening and did produce a moister cake with a longer shelf life, but liquid oils are not well suited to the formation of good, persistent foams since their low viscosity could not sustain the bubble structure the way a more viscous plastic lipid phase could. Finally, it became a situation of “surfactants to the rescue!” It was found that dissolving certain surfactants in the liquid oil before adding it to the batter could produce high ratio (lots of sugar) cakes with good volume, fine crumb, and excellent shelf life. The cakes can be mixed in a one-step process involving a slow initial mixing speed to thoroughly blend together the ingredients followed by a vigorous mixing speed to incorporate the air.

A number of food emulsifiers have been found useful for this application, mostly being the α -tending class, because of their tendency to solidify in a stable α -crystalline form within the matrix of the cake batter. Those most commonly used commercially today include AcMG, LacMG, and PGMS. The structures of those materials are illustrated in Figure 13.3. Other emulsifiers such as Polysorbate 60, SSL, and sucrose esters will accomplish the same purpose, but the most widely employed materials are AcMG and PGMS. Other emulsifiers may be added to the cocktail to enhance the performance of those two or provide other “services.”

Although all of the emulsifiers mentioned will adsorb at interfaces, liquid–air or liquid–liquid, and reduce the corresponding interfacial tensions, their activity in cake batters and the like is not directly related to that effect. In fact, their effectiveness is more related to their tendency to “solidify” and form solid barriers to isolate the lipid phase from the incipient air bubbles, which are stabilized by the proteins present in the flour, milk, and egg whites. Without that protection, the oil would destabilize the incipient foam and produce an unacceptably flat product.

As mentioned earlier, in the surfactant universe, like our “real” world, diversity can often (usually) provide unexpected beneficial effects. For that reason, it is quite often found that the use of two or more surfactants in an application rather than a single material in larger amounts can result in a significantly improved result.

13.2.3 Emulsifier Use in Dairy and Nondairy Substitutes

Milk is a protein-stabilized O/W emulsion. The presence of protein at the O/W interface obviously stabilizes that emulsion system, but their presence also complicates the process of trying to scientifically understand all of the chemical processes involved in the world of products derived from milk and milk-related products. That understanding is further complicated with the addition of one or more of the food emulsifiers introduced above into the mix. The following discussion will try to break down a little what is understood on some important aspects of milk/dairy product processing in terms of the physical chemical questions without trying to provide a truly comprehensive introduction to the subject. That is left to the references cited in the Bibliography.

13.2.3.1 What Makes Milk “Milk”?

The proteins found in milk are divided into two groups: casein and whey proteins. Casein, the protein that is coagulated in the process of making cheeses, is a complex mixture containing four major proteins: α_{S1} -, α_{S2} -, β -, and κ -casein. The proportions of each component are 4 : 1 : 4 : 1. The molecular weights range from 24 000 Da for β -casein to 121 000 Da for α -casein. To further complicate things, the caseins aggregate to form micellar structures, and those structures have molecular weights up to approximately 1×10^9 Da. The casein can be dissolved in alkaline water and dried to produce sodium caseinate, which has a molecular weight in the range of 250 000.

In whey, the main proteins are α -lactalbumin (17 000 Da) and β -lactoglobulin (45 000 Da). There are numerous other proteins present in minor amounts. The picture, from a surface chemical point of view, is further complicated by the fact that the proportion of hydrophobic to hydrophilic amino acids present varies greatly from one to another. As a rule (general, not hard and fast), it is found that the relative amounts of hydrophobic amino acid residues increase as the molecular weight of the protein increases. Taking those variations in size and amino acid content into account, it is not surprising that the surface chemical behavior of the various protein components also varies significantly. The behavior of whey proteins is significantly different from that of sodium caseinate, which also differs from β -casein. When all the different possible combinations of proteins at interfaces in milk are considered, it should not be surprising that the interfacial chemistry of milk is so difficult to understand.

The lipid portion of milk, the milk fat, is produced and protected by another complex membrane composed of a combination of proteins. That membrane varies from species to species, but only cow's milk will be considered here. The diameters of the fat droplets in native milk range from 0.2 to 20 μm , with approximately 90% being in the range of 1–8 μm and the average being about 3 μm . Since the droplets are less dense than the aqueous protein solution, they will “cream” or rise to the top if the milk is allowed to stand undisturbed for much time. Because of their protective membrane, however, the droplets will be slow to coalesce and can be re-dispersed with relative ease. In commercial milk, the fat content is standardized by removing the excess above the required level by centrifugation to produce products with 0, 0.5, 1, 2, or 3.5% fat content.

After the fat content is determined, the milk is homogenized to reduce the average droplet size from 3 to less than 1 μm . Up to this point, the interfacial chemistry of the milk has been manipulated in its “native” state. As the average droplet size is reduced by homogenization, however, there is a great amount of new interfacial area being produced, which must be stabilized by the addition of more protein. About 95% of the new interfacial area is stabilized by casein, either in the form of individual casein molecules or in the form of distorted casein micelles. Some whey proteins may be incorporated into the stabilizing membrane. Whey proteins that have been denatured form complexes with the casein proteins that are easily adsorbed into the protective membrane structure. Once adsorbed, the protein membrane structure is very stable. Because of the multipoint adsorption mechanism involved, the desorption of the proteins is very slow. There is also some evidence that the casein–whey protein complex can produce some cross-linking between adsorbed species, further stabilizing the membrane structure. With all of those proteins swimming around to adsorb at water–fat interfaces, “normal” modern homogenized and pasteurized milk does not really need help from the outside, so to speak.

Newer forms of milk such as ultra-high temperature (UHT) pasteurized or reconstituted milk, on the other hand, do receive additional stabilization help from emulsifiers of the surfactant type and emulsifying salts. Although they will not be discussed further here, emulsifying salts include such things as Na^+ , K^+ , or Ca^{2+} salts of citric or tartaric acids or phosphates (orthophosphates and polyphosphates).

13.2.3.2 Surfactant Uses in Cheeses and Cheese Substitutes

Naturally aged cheeses do not, in general, use incorporated emulsifiers, but rely on the skills of the expert cheese maker in terms of making, storing, and aging a good cheese that has the flavor, texture, and shelf life expected by a discerning consumer. In the modern cheese world, however, such attention to detail carries with it a significant cost. For a more accepting mass market, some natural cheeses may be pasteurized in order to extend their shelf life, a process that may involve the addition of additives that help ensure a standard in quality and shelf life. In addition, cheeses termed “processed cheeses” are now common.

In a processed cheese, grated ripened cheeses of various varieties and degrees of aging are mixed in determined proportion and processed in the presence of emulsifying salts to yield the processed cheese or in some cases a processed cheese spread having enhanced shelf life, desired melting characteristics, characteristic mouthfeel and spreading texture, etc. The processed cheese spreads are formulated to have higher milk fat and moisture content so that it spreads smoothly during application. The stability of the fat emulsion droplets is primarily controlled by casein. Emulsifiers may be added to obtain a smooth texture, reduce microbiological growth, and lower the amount of emulsifying salts required to obtain a high-quality cheese.

13.2.3.3 Surfactant Use in Deserts and Yogurts

Dairy and dairy-like desserts can be described as being aerated desserts, such as mousse, and non-aerated desserts, such as custards. For the aerated products, emulsifiers are essential since they are responsible for aiding the incorporation of air, ensuring that the air bubbles introduced are small and generally monodisperse and, of course, ensuring that they are stable and do not grow during storage. They also contribute to a creamy mouthfeel. Gums and starches play a more important role in non-aerated desserts, in which they control thickening, gelling, and mouthfeel.

Natural yogurt is produced by bacterial fermentation of milk. The fermentation of lactose (milk sugar) into lactic acid gives yogurt its characteristic gel-like texture and taste. The yogurt “purist,” of course, frowns on the addition of emulsifiers or other additives. The mass commercial market for yogurt-based products, however, would be in trouble without their assistance. Emulsifiers are added to assist with fat dispersion, improve mouthfeel and creaminess, and help control microbial growth.

13.2.3.4 Butter and Margarine

Making butter from the cream that rises to the top of fresh milk is a technique that has been known for thousands of years, although it has only been in the last 100 or so that we knew exactly what was involved in the process. The butter fat in cream is present as an O/W emulsion like the milk. However, the concentration of the dispersed phase in cream is much higher than the 3.5% or less in the final milk product. When the cream is “churned,” it is agitated vigorously during which time the fat globules are forced together. The force acting on the globules as they collide is enough to distort and displace the protective protein interfacial barrier, and when that occurs, the contacting fat particles are driven by surface tension effects to coalesce into a larger droplet with less interfacial area to be protected. As the churning action is continued, the system undergoes a phase inversion in which the former continuous aqueous phase becomes the now dispersed phase and the once dispersed lipid phase becomes the continuous phase, and so butter is born. No outside chemical intervention is required for making butter.

Margarine is a different story, on the other hand. It was originally developed in France in 1869 as a cheap substitute for butter after a development challenge by Napoleon III. The name actually comes from what was identified in 1813 as the basic fatty acid in animal fats, “margaric acid.” That

was later shown to actually be a mixture of stearic and palmitic acids. The butter substitute was originally called “oleomargarine,” a term that can still be heard at times, but finally shortened to just margarine. Today, margarine is a major product around the world. After its introduction in the United States in the 1930s, its use slowly increased, probably because it was significantly less expensive than butter. Its market share peaked during World War II due to butter shortages but continued to lead the market until the 1970s. After many years of not having access to much butter or avoiding it because someone decided that it was healthier than butter, margarine has developed a following based on its own virtues. It is a W/O emulsion like butter, but it is made using partially hydrogenated vegetable oil instead of butter fat. The oil phase must meet certain standards such as a specified solid fat content so that it is solid under temperature conditions like butter. The water phase is constituted using nonfat dry milk solids with the addition of salt and flavors. The exact composition of margarine is tightly controlled by national food quality and safety organizations, but in general it must have a minimum of 80% fat. The “lite” varieties obviously contain considerably less fat.

Although the margarine uses milk solids and whey proteins in the aqueous phase, those components are not enough to make a W/O emulsion that would satisfy consumer demands for a butter-like product. For achieving that end it is necessary to add emulsifiers. In most margarines, mono- and diglycerides, lecithin, or a combination is dissolved in the oil phase before the water solution is added. Some other oil-soluble ingredients such as vitamins and colorants will be added at this time. While the aqueous phase is gradually added, the mix is stirred to form the emulsion. Once emulsified, the dispersion is cooled in a heat exchanger called a “votator,” where it is further agitated and kneaded to produce the final smooth, finely dispersed W/O emulsion. In margarine, as in butter, the W/O emulsion is not particularly stable as a liquid, but since they are both usually kept at a relatively low temperature, the solid nature of the external fat phase essentially “freezes” the dispersed droplets in place and prevents coalescence.

13.2.3.5 Whipped Cream and Nondairy Whipped Toppings

Moving up the scale of simplicity from basic milk, the discussion will now turn to the role of emulsifiers (if any) in whipped cream and nondairy whipped toppings. As an alternative to regular whipped cream, vegetable oil-based imitation cream is available with a standard or low-fat content. The structure of nondairy cream is very similar to the fat and air structure of ice cream. Emulsifiers are used to produce and maintain air bubbles, resulting in a stable product with the desired texture.

Whipped cream is a foam in which the air bubbles are stabilized by agglomerated fat globules. During the early stages of mixing, air is incorporated into the cream and divided into large bubbles. Fat globules concentrate at the air–water interface and stabilize the bubbles. This process involves the partial removal of the membrane stabilizing the fat globules, exposing some fat, and forcing it into the air phase. At the same time, fat globules in the aqueous phase agglomerate, partly through membrane interactions and partly through binding of membrane protein to milk proteins. The fat globules must agglomerate but not coalesce as they do during the churning of butter. Thorough cooling of the cream solidifies the fat to prevent coalescence. If the cream is too warm while being whipped, butter may be the end result. Most of the air is incorporated at the beginning of the mixing process, before the cream acquires too much viscosity. Further mixing shears and divides the already incorporated air bubbles, and the newly formed air–water interface is stabilized by the agglomerated fat globules. The viscosity increases as a result of the increased number of smaller air bubbles and continued agglomeration of fat globules to form a network throughout the system. As viscosity slowly develops, the shear stress on the air bubbles increases, leading to further subdivision, and the whipped cream becomes stiff, which is usually the desired endpoint for making whipped cream.

Emulsifiers may be added to the cream to increase “overrun” and increase the final stiffness. Overrun is a measure of the volume of the final product compared with the volume of the starting cream, the difference being the amount of air incorporated. For normal whipped cream, the overrun is usually 100%. It has been found that if emulsifiers are added to cream, the overrun and stiffness can be significantly increased. A 50–50 mixture of Polysorbate 60 and Polysorbate 65 at a 0.5% concentration produced a whipped cream with 200% overrun. If Polysorbate 80 (the oleate ester) was used instead of 60, a lower overrun and softer whipped cream results. Monoglycerides alone are not generally found to be effective aerating agents, although a mixture of GMS with its citric acid derivative can produce a very stiff foam with a high overrun. Lactylated GMS also produces stiff foams with high overrun, which may have resulted from its tendency to form strong, viscous interfacial films.

Consumers have traditionally had four concerns about using real cream for whipping: the cost, the high level of saturated fats in milk fat, the cholesterol content, and the work required to actually do it. The first and last are simply yes or no questions. Do you want to pay the extra cost and do the extra work to have “real” whipped cream? The middle two are questions about opinions: Do you really eat enough whipped cream for those supposed, and now pretty much debunked, “health” issues to really matter? Nondairy whipped toppings, after all, contain significant amounts of saturated fats plus other “additives” to make the real thing look like a miracle elixir. But then, most consumers tend to follow TV or newspaper “doctor” trends instead of using their own common sense.

Putting such concerns aside, producing nondairy whipped toppings with vegetable fats (a.k.a. partially hydrogenated vegetable oil) is a complicated process. Unlike natural cream, the vegetable fats do not contain any natural emulsifiers, so the necessary emulsifying capability must be added during production. But the process is not a matter of simply mixing some fat and emulsifier with water containing some dissolved protein in a pot and whipping the mixture. For the system to produce an acceptable whipped product, the “fat” must have the proper solid fat profile so that the correct amount of solid fat is present to stabilize the air bubbles. Remember that liquid oils destabilize foams. Also, the emulsifier used must interact with the dissolved protein to produce the necessary degree of protein desorption to give the required degree of control over desorption of the protein layer. Finally, the emulsion may be spray-dried for storage and then reconstituted with cold water before whipping. The emulsifier, protein, and any other ingredients such as sugar, flavors, and thickeners like maltodextrins must be able to rehydrate in the proper way to produce an emulsion that will actually whip into the desired foam structure. In short, developing a good nondairy whipped topping is not simple science.

A basic whipped topping powder formula contains 25% partially hydrogenated vegetable fat and 5% emulsifier melted together and 50% water containing 15% maltodextrin and 5% sodium caseinate. The maltodextrin is added as an aid to the production of a good-quality spray-dried powder, to coat the powdered components to prevent clumping or coalescence, and to aid in a smooth regeneration of the original emulsion. The two phases are mixed, homogenized, and then spray-dried. The emulsion is stabilized by the combined effects of the emulsifier and proteins. After drying, the powder is usually held at 5 °C for at least an hour to solidify most of the fat and then stored at temperature no higher than 20 °C.

For whipping, the powder is dispersed in an equal weight of cold water. Agitation initiates many of the same processes that occur during whipping dairy cream – fat globule agglomeration, partial desorption of protein from the fat–water interface, air incorporation, stabilized by fat globules, and air division to form a stable foam.

The nature of the fat seems to be crucial. Best results are obtained with partially hydrogenated vegetable oils such as coconut or palm kernel oils combined with soybean or sunflower oil. The

first two materials are termed “lauric” fats because they contain a larger amount of C_{12} fatty acids than the latter. The proposed mechanism of the foam stabilization process is thought to be related to the interaction of the hydrophobic portions of the stabilizing protein barrier, the lipid phase, and the emulsifier that produces partial desorption of the protein from the fat–water interface to produce agglomeration without actual drop coalescence.

It is felt that the hydrophobic portions of the adsorbed protein penetrate the fat droplet and inhibits its crystallization even though it is below its normal crystallization temperature. In essence, the fat is in a “supercooled” state. When the emulsifier displaces the protein from the droplet, the fat should immediately crystallize. Crystallization concurrent with protein desorption would seem to be necessary to have agglomeration without drop coalescence and concentration at the air–water interface to stabilize the foam. The essentially simultaneous events – agglomeration and crystallization – seem to be related to the presence of short-chain C_{12} hydrophobic chains in the fat molecules. It occurs in the presence of C_{12} fats, but not with primarily C_{18} fats. A partially or fully hydrogenated C_{18} fat does not seem to exhibit the supercooling phenomenon and produces a poor whipped topping when used alone. A high C_{12} fat, which will normally have a low melting point, will exhibit little or no fat crystallization and will also produce an unacceptable foam. A proper mixture of the two fats, on the other hand, seems to work well.

α -Tending emulsifiers such as PGMS or lactylated monostearate seem to perform well in this application as does Polysorbate 60. Both types of emulsifiers produce a relatively thick layer at the fat–water interface. The α -tending emulsifier layers are thick because they are multilayer structures. Polysorbate 60 produces a thick adsorbed layer because of the water bound to the POE chains. Those properties are assumed to promote partial protein desorption while at the same time forming a somewhat “sticky” interface on each fat globule that enhances agglomeration and the formation of a good, stable foam.

13.2.3.6 Dairy Drinks

In dairy products such as flavored milk, chocolate milk, and recombined milk (made from milk powder and water), emulsifiers secure the desired emulsion stability, mouthfeel, and particle suspension. They also provide stability for long-life milk (UHT treated) by preventing separation. The emulsifiers normally used are lecithin and mono- and diglycerides of fatty acids.

13.2.3.7 Ice Cream

Moving up the complexity scale of dairy products, we come to ice cream. Ice cream is probably one of the most complex food products in existence – an aerated emulsion of fat, proteins, sugars, gums, flavors, and emulsifiers containing ice crystals. Emulsifiers help provide a smooth, creamy, fine texture as well as slowing down the rate at which the served ice cream melts. They also help to reduce freezing time, improve whipping, and stabilize the air cells. Typically used emulsifiers are mono- and diglycerides of fatty acids, polyoxyethylene sorbitan esters, and sucrose esters of fatty acids.

The fundamental phenomena that occur during the production of ice cream are very similar to those observed in the production of whipped cream. As in the previous product, the primary aim is to produce a well-aerated foam system stabilized by fat globules adsorbed at (actually between) the air–water interface (Figure 13.13). However, in ice cream production, the temperature regime is different, so differences in emulsifier use might be expected.

After the initial emulsion is prepared, it is usually “aged” for 4–24 hours at $\sim 5^\circ\text{C}$. During the aging period, partial desorption of the protein around the fat globules occurs, and the globules agglomerate. Desorption is, again, aided by the presence of the emulsifiers. As in whipped

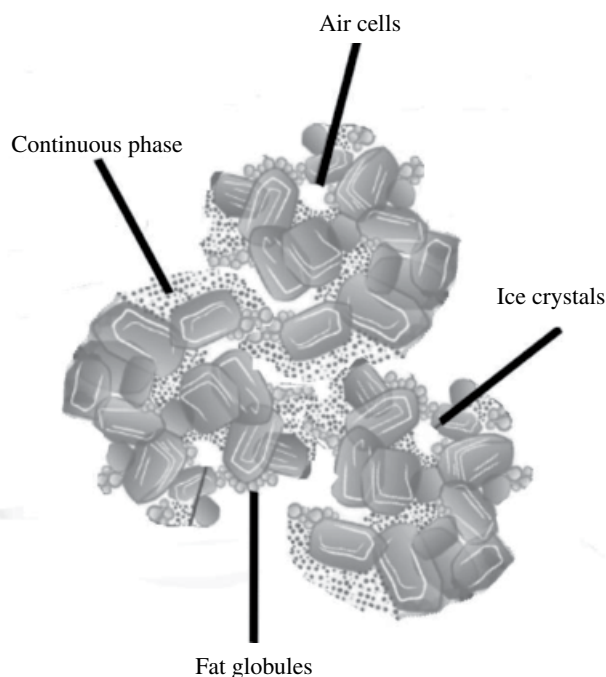


Figure 13.13 The basic structure of ice cream.

toppings, it appears that the fat becomes supercooled and solidification is related to the desorption process. During agitation and freezing, the fat particles aggregate at the air–water interface and stabilize the air bubbles. The addition of glycerol monostearate or the plastic mono-distearate increases the degree of desorption and produces a “drier” ice cream with smaller air bubbles. That phenomenon can also result in a higher overrun. Polysorbate 80 (the oleic acid hydrophobic group) also seems to work well in that sense. Even though the unsaturated hydrophobic group is not a good foaming agent for whipped toppings, probably because of the more “liquid” nature of the chains at whipping temperatures, since ice cream is processed at a much lower temperature, the oleate chains become more rigid and perform more like the stearate equivalents. In ice cream, the emulsifiers are used at levels between 0.2 and 0.4%, while in whipped toppings it is usually 3–5%.

Ice creams also usually have added vegetable gums such as guar, carrageenan, tragacanth, or CMC. Those ingredients are added primarily as crystal growth inhibitors to prevent the growth of water and lactose crystals over time. Larger crystals produce a sandy or gritty mouthfeel, especially when the product is stored for a long time.

13.2.3.8 Coffee Whiteners

A final topic of interest in the nondairy line is the modern use of coffee whiteners. Putting cream or milk in coffee is enjoyed by many people. However, today, except in very special locations, the cream pitcher has disappeared from the table, and milk, if real, is available in small plastic cups that, as often as not, “spit” on the user as they are opened. That phenomenon is not, of course, the fault of the liquid contents. More commonly, the “offending” white liquid, when stirred into the coffee, tries to mimic the effect of cream, at least in terms of lightening the color of the coffee. It does not mimic the taste of real cream, of course, but most people today do not know the

difference. For home use, coffee whiteners are usually found as spray-dried powders that rapidly dissolve when added to the hot coffee to produce the desired whitening effect.

There are a number of whitener formulations reported in the patent and industry literature, but a typical spray-dried whitener contains about 37% vegetable fat, 56% corn syrup solids, 5% sodium caseinate, 1.6% dipotassium phosphate, 0.3% GMS, 0.1% Polysorbate 65, plus flavors, and an anti-caking agent as needed. In the initial emulsion preparation, the emulsifiers are added to the fat, and the other ingredients dissolved in water and the mixture emulsified, homogenized, and spray-dried. Like spray-dried nondairy whipped toppings, the powder is held under cool conditions for a period to allow the fat to solidify completely to avoid clumping.

Coffee creamers can be found in three physical forms: liquid, frozen liquid, and powder. All require emulsion stability during storage and when used in hot coffee with a low pH. Emulsifiers facilitate the dispersion of coffee creamer and improve its whitening properties along with the creaminess of coffee. Commonly used emulsifiers for creamers are polyoxyethylene sorbitan esters, mono- and diglycerides of fatty acids, mono- and diacetyl tartaric acid esters of mono- and diglycerides of fatty acids, and sodium stearyl-2-lactylate.

The fat for coffee whiteners usually has melting point of about 42–45 °C. It has a rather steep solid fat content profile (a relatively sharp melting) so that it will melt completely and quickly at the temperature of normal coffee. In that way an undesirable fatty or waxy mouthfeel is avoided; however, it must remain relatively solid at room temperature so that the powder does not clump during storage. Corn syrup solids or maltodextrins are added to provide body during processing, help protect the fat particles during storage, and promote faster re-emulsification when added to the coffee.

The added emulsifiers serve two main purposes: during homogenization, they facilitate the formation of fine fat droplets, and, working with the proteins, they help prevent what is called “feathering,” which occurs if the regenerated emulsion breaks down and the fat separates from the water phase producing an unsightly “oil slick” on the surface of the coffee. The protein layer helps emulsify the fat, and the proper emulsifier can stabilize the protein layer when the whitener is added to the hot, acidic coffee. The protein layer can be destabilized by calcium or other divalent ions and by organic acids in the coffee. The inclusion of potassium phosphate counters that tendency. Some reports recommend the use of SSL rather than Polysorbate 65 because its protein complexing activity apparently makes the protein more effective.

13.2.4 Protein Emulsifiers in Foods

Proteins, because of the basic amphiphilic natures of their component amino acids, can be considered to be “natural” surface-active species and, not surprisingly, have served mankind as readily available emulsifiers, foaming agents, and stabilizers throughout our history. At first, of course, their use was a matter of serendipity followed by observation, trial and error, and, ultimately, careful scientific research. Today we know a great deal about how proteins work in various food products, what chemical structure elements make them good at what they do, and how to modify them to improve their utility.

Proteins are, of course, polypeptides composed of a combination of 20 “common” natural amino acids. It is a combination of what amino acids are present in the molecule and the arrangement of those units along the chain that determines the characteristics of each protein in its natural state. That natural state is generally broken down into four levels of molecular structure or conformations illustrated in Figure 13.14. In order to try to get a handle on the complex activities and functions of proteins in food products, a brief review of how they function in solution and respond to changes in their solution environment may be useful.

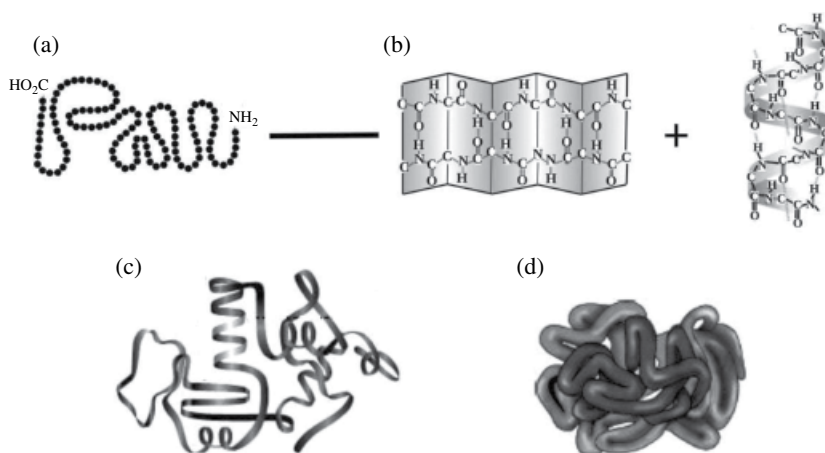


Figure 13.14 The four primary levels of protein conformations in solution (a) primary structure – the amino acid sequence, (b) secondary structure – β -sheets and/or α -helix, (c) tertiary structure, and (d) quaternary structure.

The four structures found for proteins in solution are the following:

- 1) The *primary structure* of a protein is the linear arrangement or sequence of the amino acids composing the protein chain (Figure 13.14a). That sequence basically defines the relative balance among the potentially anionic amino acids, with carboxylic acid tails on their side chains, the potentially cationic amino acids with amine-terminated side chains, and the hydrophobic acids whose side chains are terminated by hydrocarbon groups. Each strand has one end terminated by an amino acid carrying a carboxylic acid side chain, the C-terminus, and the other by a basic amino-terminated side chain, the N-terminus.
- 2) The protein *secondary structure* is defined by stretches or strands of proteins or peptides having different local structural conformations depending primarily on hydrogen bonding. The two main types of secondary structure are the α -helix and the β -sheet. The α -helix is a right-handed coiled strand (Figure 13.14b). The side-chain substituents of the amino acid groups in an α -helix extend to the outside of the chain. Hydrogen bonds form between the oxygen of the C=O of each peptide bond in the strand and the hydrogen of the N–H group of the peptide bond four amino acids below it in the helix. The intra-strand – within the same strand – hydrogen bonds make this structure especially stable.

The hydrogen bonding in a β -sheet is between strands (inter-strand) rather than intra-strand as seen in the α -helix. The sheet conformation consists of pairs of strands lying side by side. The carbonyl oxygens in one strand hydrogen bond with the amino hydrogens of the adjacent strand. The two strands can be either *parallel* or *antiparallel* depending on whether the strand directions (N-terminus to C-terminus) are the same or opposite (Figure 13.14c). The antiparallel β -sheet is more stable due to the more well-aligned hydrogen bonds.

- 3) The protein *tertiary structure* is determined by the overall three-dimensional shape of the entire protein molecule. The molecule will bend and twist in such a way as to achieve maximum stability or the lowest energy state. Although the three-dimensional shape of a protein may seem irregular and random, it is produced by many stabilizing forces due to bonding interactions between the side-chain groups of the amino acids.

Under “natural” conditions, the hydrophobic side chains of neutral, nonpolar amino acids such as phenylalanine or isoleucine tend to be buried in the interior of the protein molecule, thereby shielding them from interactions with the aqueous medium. The alkyl groups of alanine, valine, leucine, and isoleucine often form hydrophobic interactions between one another, while aromatic groups such as those of phenylalanine and tyrosine often stack together. Acidic or basic amino acid side chains will generally be exposed on the surface of the protein since they are hydrophilic. All of those possible interaction types balance together to produce the most energetically favored tertiary structure.

Covalent bonds may also define a proteins tertiary structure. The formation of disulfide bridges (R-S-S-R) by oxidation of the sulfhydryl groups on cysteine (R-SH) is an important aspect of the stabilization of protein tertiary structure, allowing different parts of the protein chain to be held together covalently. Additionally, hydrogen bonds may form between different side-chain groups. As with disulfide bridges, these hydrogen bonds can bring together two parts of a chain that are some distance away in terms of sequence. Salt bridges involving ionic interactions between positively and negatively charged sites on amino acid side chains also help to stabilize the tertiary structure of a protein.

- 4) The quaternary structure of a protein occurs when it consists of multiple polypeptide chains or protein subunits. These subunits may be the same (as in a homodimer) or different (as in a heterodimer). The quaternary structure refers to how the protein subunits interact with each other and arrange themselves to form a larger aggregate protein complex (Figure 13.14d). The final shape of the protein complex is again stabilized by various interactions, including hydrogen bonding, disulfide bridges, and salt bridges.

Because of the amphiphilic chemical structure of proteins, they tend to be surface active. While they have definite three-dimensional structures in solution, they tend to lose that structure or “denature” when they adsorb at water–air or water–oil interfaces. In that situation, the proteins essentially become polymeric surfactants as discussed in Chapter 9.

13.2.4.1 Proteins as Foam Stabilizers

Perhaps the most familiar example of foams stabilized by proteins is in whipped egg white to form meringue. The main protein in egg white, ovalbumin, is readily denatured during the formation of water–air interface during the whipping process and in that form spreads along the new interface, forming a rigid barrier that stabilizes the incipient foam. When whipped to the so-called “dry-peak” stage, essentially all of the water in the system is immobilized in the protein-foam structure and a stiff, stable system results. The water is so tightly bound that there is no drainage for a considerable amount of time. Many other proteins can be whipped to produce foams, but the resulting structures are not as stable, leading to more rapid drainage and ultimate foam collapse.

The reason for the difference in the effectiveness of ovalbumin and other proteins in foam stabilization is generally attributed to the ease with which different proteins return to their natural configuration or the reversibility of the denaturing process. Evidently, for ovalbumin, the process is essentially irreversible so that it remains effective at stabilizing the foam structure, even though it represents a very high relative energy state. Another protein that also produces reasonable foams but does not maintain the stability is soluble soy protein. It will easily unfold during the whipping process but also seems to easily return to the aqueous phase and to its native configuration, which allows drainage and subsequent foam collapse. Investigations have shown that if the soy protein is acetylated to convert the charged lysine groups to uncharged acetamido groups, the material can be whipped into a reasonably stable dry-peak foam similar to that produced by ovalbumin.

Another important application of foaming proteins in foods is related to cake batters. In that application, the soluble proteins in the flour, along with any egg whites that may be used, act as foaming agents. If oils or other fatty material is present, the proteins remain the primary foaming agent even though some portion of it may be occupied emulsifying and stabilizing the dispersed fatty material. The destabilizing process of the foams in batters with oil present must usually be controlled by adding an α -tending emulsifier that will adsorb at the surface of the oil droplets and prevent it from destabilizing the foam.

13.2.4.2 Proteins as Emulsifying Agents

As mentioned, proteins have a primary structure that is constituted by the sequence of amino acid groups along the chain. Since those groups may be hydrophilic or hydrophobic, the sequence will essentially define the most favorable way for the protein chain to coil up (its secondary structure) with, as far as possible, the hydrophilic groups pointing out into the water phase and the hydrophobic groups tucked into the interior of the coil as far away from water contact as possible. The coiled intramolecular “micelle” structure of the native protein is not rigidly fixed, of course, and can unfold when it encounters a favorable environment. If a water–oil interface is present, the energetics become favorable for the chain to uncoil and expose the “hidden” hydrophobic chains to the oil side of the interface and adsorption occurs. The hydrophilic groups, of course, remain in the aqueous phase, and a rather rigid, viscous interfacial barrier is formed to stabilize the emulsified oil droplets. The situation is represented schematically in Figure 13.15.

Water solubility is not a limiting prerequisite for a protein to be an effective emulsifier. Proteins with low water solubility such as myosin present in meats are effective at emulsifying fat during the grinding process for making sausage, for example. Other proteins, such as isolated soy protein, are often added to the mix to help emulsify the fat while also serving to bind water and add weight to the finished product. Other important protein emulsifiers are found in mayonnaise and similar dressings.

From a physical chemical standpoint, it should be kept in mind that the rate at which a water–oil system reaches its minimum interfacial tension depends on the speed at which the emulsifier can diffuse to the interface and attain the molecular orientation needed for stabilizing the system. The diffusion rate of a molecule in solution, all things being equal, will depend on the size or molecular

Soluble globular configuration

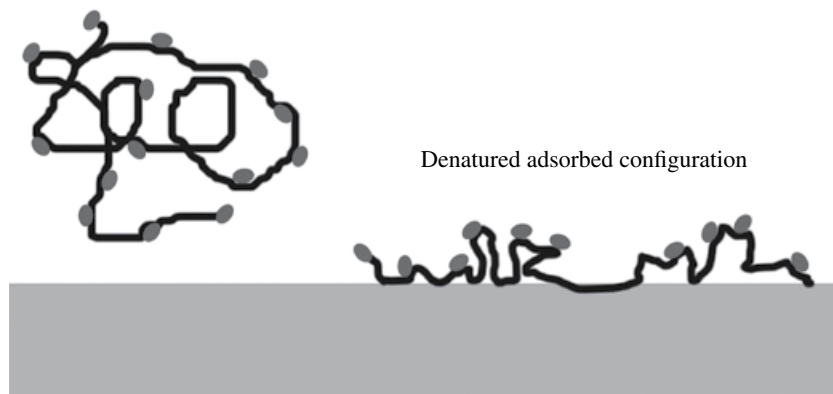


Figure 13.15 Configuration changes in soluble protein emulsifier going from soluble to adsorbed condition.

weight of the diffusing molecule. A typical non-polymeric emulsifier may have a molecular weight of 300 or so, while a typical protein may be from several thousands to several hundreds of thousands. A typical surfactant will diffuse to an interface and orient itself within seconds. A high molecular weight protein, on the other hand, may take up to an hour or more to reach the interface, uncoil to expose the hydrophobic side chains and fully adsorb.

13.2.4.3 Protein–Low Molecular Weight Emulsifier Interactions

As was discussed in Chapter 9, polymers, including proteins, and low molecular weight (LMW) surfactants can and often do interact in solution. Those interactions may involve what may be termed “complexation,” where there are specific interactions between the two in solution, or “competition,” where the interaction takes place at the interface itself. As noted above, if protein and a typical emulsifier are present in a system and new interface, either water–oil or water–air, is created, the LMW emulsifier, if present in a concentration above its **cmc**, will generally diffuse and adsorb at the interface more rapidly than the large, slower-moving protein molecule. That initial adsorption, however, is reversible in that individual molecules can come and go somewhat randomly. However, with time, the protein will diffuse to the interfacial region and unfold to expose the hydrophobic side chains, which can then displace adsorbed LMW emulsifier. Since the protein will have a number of hydrophobic side chains available, it will be able to anchor itself firmly at the interface at many attachment points, essentially saturating the available interfacial area and “locking out” the LMW emulsifier. That is, the adsorption of the protein will be essentially irreversible. That image is interesting as an initial concept, but things are seldom that simple in the world of surface activity. If both protein and LMW emulsifier are present, several interactions may take place:

- 1) Competitive adsorption in which the two surface-active molecules compete for available interfacial area.
- 2) Displacement in which the more surface-active compound displaces the less active one from the interface.
- 3) Enhancement in which a complex of the smaller molecule with the protein increases the interfacial activity of the protein.
- 4) Reinforcement in which interaction at the interface results in more efficient packing of the elements involved, in this case the hydrophobic side chains of the protein, increasing the total concentration of surface-active elements at the interface and possibly lowering the interfacial tension even more.

In a given emulsifier–protein combination, more than one type of these interactions can be observed depending on the conditions. They seem to be more common in foam systems although they also can be identified in emulsions. Although investigations into every class of LMW surfactants and most types of proteins have been carried out, most relate to the interactions of anionic and nonionic emulsifiers.

In terms of surface tension lowering, proteins are usually more effective in the presence of added LMW material below its **cmc**. It is usually found that the minimum surface tension achieved will be the same as in the absence of any added LMW material. Once that concentration is passed, however, the LMW material usually becomes the dominant species, and the surface tension lowering will be that seen for the LMW material in the absence of protein. That effect may be delayed somewhat, however, due to the slower process of displacement of the protein molecules by the LMW surfactant. In cases where the LMW emulsifier binds to the protein to form micelle-like structures associated with the hydrophobic portions of the protein chain, it may be found that the complex enhances the rate or extent of chain unfolding, opening

up the chain and allowing for faster adsorption at the interface. In the case of a water–oil interface, the presence of a protein chain will produce a more viscous interfacial film, which will provide greater strength to the stabilizing structure of the emulsion. As is often the case with respect to surfactant interactions, however, things are seldom as simple as they seem. If an added LMW emulsifier is particularly surface active in a given system, it may over time displace the adsorbed protein film and reduce the favorable film viscosity, thereby reducing the stability of the emulsion.

13.3 Pharmaceutical and Medicinal Applications

Many pharmaceutical products have limited solubility in water, so it is often necessary to use some mechanism to improve that solubility in order to facilitate their bioavailability in various pharmaceutical formulations. One obvious method for improving drug delivery is the use of surfactants to reduce the interfacial tension between water and liquid drugs and their carriers. The use of surfactants is necessary to reduce the interfacial tension between the aqueous medium and the drug and/or its water-insoluble vehicle, if present. That, of course, will facilitate the preparation and stability of emulsified systems. Another approach is the use of micellar systems to solubilize the drug in the micelles. Dispersed solid drugs need surfactants to maintain the disperability of the particles and retard or prevent irreversible particle agglomeration or coalescence in storage so that they can be easily re-dispersed for use after possible sedimentation during storage. In addition, surfactants find use in various medicinal applications as aids to the transport of the active species through the skin, rectovaginal and urethral membranes, and other systems to increase the rate of percutaneous absorption. Surfactants are also used in dental, oral, and sublingual applications. They are used to produce creams, gels, and ointments. They are important for transdermal patches and in tapes and other skin applications. In short, surfactants are used in pharmaceutical and medicinal applications to emulsify, disperse, solubilize, and transport medicinal ingredients just as they are in so many other modern applications.

Surfactants are also widely used in molecular biology in formulating new and in modifying existing medical preparations, in the production of proprietary medicines, in the production of chemical preparations aimed for the domestic use, etc. All this is understandable since the properties of surfactants are to some degree responsible for the existence and the performance of cellular membranes, emulsification, solubilization, and transport of compounds that are otherwise insoluble in living tissues. Surfactants also function as film formation promoters, wetting agents, detergents, bactericidal agents, etc.

Because of their unique functional properties, surfactants find a wide range of uses in pharmaceutical preparations. These include, depending on the type of product, improving the solubility or stability of a drug in a liquid preparation, stabilizing and modifying the texture of a semisolid preparation, or altering the flow properties of a granulate, thus aiding in the processing of the final tablet dosage form. In addition to their use as additives to improve the physical and chemical characteristics of the formulation, surfactants may be included to improve the efficacy or biological performance of the product. The properties of surfactants are such that they can alter the thermodynamic activity, solubility, diffusion, disintegration, and dissolution rate of a drug. Each of these parameters influences the rate and extent of drug absorption. Furthermore, surfactants can exert direct effects on biological membranes, thus altering drug transport across the membrane. As is often the case in biological systems, the overall effects of the inclusion of one or more surfactants in a pharmaceutical formulation can often be quite complex and go beyond the initially intended

goals for their use. As one example, surfactants may reduce the effectiveness of antimicrobials or preservatives included in a formulation.

The surfactants that are used in pharmaceutical applications fall into the standard surfactant classifications: anionic, cationic, nonionic, and amphoteric. The material of choice will depend on the characteristics of the target system and the biocompatibility of the surfactant in that specific application. Fatty alcohol ethers, $\text{RCH}_2\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$, where n is the average number of polyoxyethylene units in the hydrophilic chain, are one of the more commonly used nonionic surfactant families. Sorbitan esters (Spans) are also widely used, especially for W/O emulsions because they have low water solubility and low HLB numbers. They are also used as wetting agents in some applications. The ethoxylated sorbitan esters (Tweens or Polysorbates) have relatively high HLB values (>12) and are employed as O/W emulsifiers, solubilizers, dispersants, and wetting agents. They are also used in the manufacture of drug emulsions, suppositories, creams, gels, foams, tablets, and capsules. The most commonly used are Polysorbate 20 (sorbitan monolaurate) and Polysorbate 80 (sorbitan monooleate). Polymeric nonionics such as polyoxyethylene–polyoxypropylene block polymers (POE-POP), commonly referred to as poloxamers and commercially known as Pluronics, among other names, have also found wide acceptance in pharmaceutical applications. Their great advantage, aside from their basic utility as surfactants, is that the physical characteristics (solid, paste, or liquid), average molecular weight, and best probable HLB balance can be readily estimated from the “Pluronic grid,” which gives all of the pertinent information on each product so that a good estimate of the correct POE-POP balance and other characteristics can be made directly and a great deal of trial-and-error time and money can be saved. The “code” for the grid was introduced in Chapter 9. Nonionic surfactants are usually preferred for use in human applications. They are generally milder and more bio-friendly than charged surfactants, although at times a charged species will be necessary or even advantageous.

Some pharmaceutical drugs exhibit surface activity based on their chemical structure. Early tricyclic antidepressant drugs are one such class of materials, but they have pretty much been supplanted by more effective and less potentially dangerous drugs. Surface-active proteins are found in many biological systems where their absence can result in serious and even fatal system failures. An important example is found in many premature infants, who may develop serious breathing difficulties because their lungs do not produce a sufficient amount of the required natural protein surfactant. Today, the use of aerosolized surfactant solutions, including proteins, can treat the problem without the use of invasive and stressful intratracheal procedures for relieving the problem.

13.4 Petroleum and Natural Gas Extraction

The worldwide push for the development and use of “renewable” energy sources notwithstanding, the extraction of petroleum and natural gas from underground deposits remains vital to our ability to ensure an adequate and reliable energy source for the needs of our technological world. Since the time of the first big oil crisis in 1967, more political than technological in nature, vast amounts of effort have been devoted to finding better ways to access the oil and gas reserves currently identified, to maximize the efficiency of the processes available, and to find new processes that do an even better job by making available deposits that are not economically viable without the introduction of new technology.

One of the important elements leading the charge in improving our abilities to reach and exploit the deposits identified is that of the application of surfactants and related systems to “open up” the

natural structures of the geological deposits and allow for the safe and efficient extraction of fluid hydrocarbon resources. This section is a quick snapshot of some of the applications of surfactants and related surface-active systems in that search.

13.4.1 Enhanced Oil Recovery

Although the maximum recovery of mineral resources from known deposits and reserves has always been a goal of those in the industry, it is only since the onset of the oil crises of the 1970s that vigorous scientific efforts outside the petrochemical industry have become of importance. A review of the fundamental and applied surface chemical literature during the last 40 years illustrates the rapid growth in the number of patents, scientific publications, books, and reviews that address the problems of resource recovery and possible solutions. Although an in-depth discussion of the present state of knowledge in the field of secondary and tertiary oil recovery is not possible here, it is useful to introduce the major mechanisms for attaining petroleum recovery enhancement that are related to surfactants.

Initial or primary oil recovery is accomplished primarily by use of the inherent energy of the oil reservoir, that is, the pressure of the gases and volatile hydrocarbons trapped under high pressures and temperatures in the rock formation. For shallow wells, mechanical pumping may be used. Additional recovery may be accomplished by the injection of water or steam into the rock to maintain a high pressure in the system and force additional oil to the surface through production wells. The use of such mechanisms can normally result in the recovery of about 40% of the potential oil in the formation. Beyond that point, more drastic (and more expensive) measures must be employed. Such measures may involve the use of surfactants and polymers for the alteration of the interfacial and rheological properties of the oil deposit and the fluids injected to aid in moving the crude toward production wells.

There are four primary mechanisms by which enhanced oil recovery can be attained through the use of surface-active additives: (i) the production of very low ($< 10^{-3}$ mN/m) interfacial tension between the oil and the aqueous flooding solution, (ii) the spontaneous emulsification or micro-emulsification of the trapped oil, (iii) the reduction of the interfacial rheological properties at the oil–aqueous solution interface, and (iv) control of the wettability of the rock pores to optimize oil displacement.

A major role of low interfacial tensions in enhanced oil recovery is to facilitate the removal of small oil drops entrapped in pores that have been wetted by water. The interfacial tension between water and a common crude oil is about 30 mN/m, and typical pore sizes may be in the range of 10 mm, so the capillary pressure, as calculated with Eq. (12.10), retarding flow of the trapped oil will be greater than the normal pressure gradients encountered in oil formations. In discussions of liquid flow through capillary systems, it is common to refer to the “capillary number,” which is the ratio of the surface tension of the liquid to its viscosity. A small capillary number implies easier flow through the system, so a reduction in interfacial tension should produce an improvement in oil extraction.

“Spontaneous emulsification,” as the name implies, refers to the formation of small drops of oil in the aqueous flooding solution in the absence of mechanical agitation. Assuming pore sizes of approximately 10 mm, it is clear that the formation of drops of a 1–2 mm diameter or less should facilitate the flow of oil in the system. Since mechanical agitation in an oil reservoir is obviously impractical, the emulsification process must require a minimum of energy input. This energy is usually supplied by the diffusion of water-soluble components from the oil to the aqueous phase, resulting in the creation of turbulence at the interface and emulsification.

In Chapters 10 and 11, it was noted that one mechanism for the stabilization of emulsions, foams, and other fluid interfaces was the presence of a viscous or elastic interfacial layer. The extraction of oil from porous rock formations with varying pore sizes requires the expansion and contraction of O/W interfaces. The presence of a highly viscous interfacial layer could greatly inhibit such action. Because oil deposits naturally contain surface-active components that adsorb at the O/W interface, such elastic films are commonly encountered. To counteract their effect, it is necessary to displace the elastic interfacial film with one possessing more favorable interfacial rheological properties.

One of the major areas of research into enhanced oil recovery has been the modification of the wetting characteristics of oil-bearing rocks by the addition of surface-active materials. In this case, the goal is to enhance the extent and rate of wetting of the rock by aqueous solutions so that the petroleum deposits can be more efficiently displaced by water pumped into the formation. It may also be that wetting phenomena could be used to assist in mechanically breaking or fracturing the rock formation to produce larger pores and, as a result, facilitate oil removal. Unfortunately, the very nature of oil-bearing rock formations means that there may be great variations in the surface characteristics of the pore surfaces, wide differences in wettability, and significant differences in the requirements for the appropriate wetting agent.

In addition to the four mechanisms for surfactant action in enhanced oil recovery cited above, work continues on the use of polymeric additives to control the rheological properties of the aqueous flooding solutions. In the use of such processes in conjunction with surfactant additives, it is important to consider potential interactions between the polymer and the surfactant. As more surface-active chemicals are employed in the recovery process, control of the formation and breaking of emulsions and microemulsions produced in the recovery process can become important as a postproduction problem.

A new area of research related to oil production is the use of biosurfactants. The use of such materials is so far limited by cost and availability, but work is currently being carried out on the *in situ* production of such materials by selected microorganisms. Such underground production, while conceptually interesting, carries with it a number of significant problems, not the least of which is finding organisms that can survive and flourish under the harsh environmental conditions found in oil deposits. Nevertheless, hardy organisms are being discovered and/or developed every day, so the not too distant future may see significant developments in that area.

In view of the foregoing observations, and in consideration of the sometimes harsh chemical environments present in oil reservoirs, a number of points must be considered in the selection of suitable oil recovery surfactants. Some of those factors are (i) the production of a low O/W interfacial tension; (ii) the compatibility of the surfactant with other additives such as polymers; (iii) the long-term chemical stability of the surfactant under the conditions encountered in the oil-bearing rock (temperature, pressure, etc.); (iv) the activity of the surfactant under the conditions of use, including the salinity or electrolyte content of the aqueous phase; (v) the solubility characteristics of the surfactant in the oil and water phases, including mesophase formation, cloud points, Krafft temperature, etc.; (vi) potential environmental impacts; and, of course, (vii) economics.

In principle, the physical concepts discussed in earlier chapters and above for the adsorption and activity of surfactants at L/L and S/L interfaces will apply equally well to crude O/W interfaces and porous rock deposits. Unfortunately, the reality of the situation is such that the best laboratory models of oil-bearing rock formations only qualitatively reproduce what is found thousands of feet below the surface. As a result, the general principles that work so well for emulsification and detergency fall short of answering many of the questions that arise in an actual petroleum recovery situation. In addition, reservoir conditions and crude oil characteristics differ greatly among Texas,

Saudi Arabian, and North Sea fields so that components effective in one area may perform less well in others. As a result, a great deal remains to be learned before we can take full advantage of the potential for surfactants to increase the availability of petroleum resources to fuel our technological development.

13.4.2 Hydraulic Fracturing or “Fracking”

A relatively new and widely employed technique for enhancing the recovery of difficult to access oil and gas reserves is through hydraulic fracture, better known to the general public as “fracking.” Hydraulic fracturing is a technique for stimulating the flow of oil or gas in a well in which rock is fractured or broken open by the injection of a pressurized liquid. The process involves the high-pressure injection of a “fracking fluid” into a wellbore to create cracks or open cracks already present in the structure of the deep-rock formations through which natural gas, petroleum, and brine will flow more freely. Fracking fluids are primarily water mixed with sand or other solid mineral or ceramic particles called “proppants” suspended in the fluid with the aid of thickening agents. The most common proppants are sand (SiO_2) and aluminum oxide (Al_2O_3). When the hydraulic pressure is removed from the well, small grains of the proppants hold the fractures open, maintaining the flow of oil and gas.

In many, if not most, fracking fluids, surfactants are included to improve the efficacy of the crack opening process and “lubricating” the opened cracks to enhance the flow of oil, gas, or brine through the system. It is hard to pin down the exact kinds and levels of surfactants employed since the composition of the fluid will vary according to the characteristics of the geological formations being exploited.

The use of fracking for oil and gas recovery is a controversial topic from both ecological and geophysical points of view. Hydraulic fracturing is highly controversial in many countries and may be banned in the EU. Its proponents point out the economic benefits of having greater access to known, but currently difficult to exploit, hydrocarbon reserves. Opponents, on the other hand, argue that these potential benefits are outweighed by the potential environmental impacts of the process. Claimed real or potential risks include the contamination of ground and surface water, air and noise pollution, and the triggering of earthquakes, along with the consequential hazards to public health and the environment. Then there is, of course, the blanket opposition to possibly increasing dependence on burning hydrocarbon fuels instead of increasing emphasis on renewable energy sources.

Direct methane leakage is also a potential problem directly associated with hydraulic fracturing, where some measurements report the leakage rate in some areas where fracking is used to a significant extent, estimated to be about 10%, or over five times the officially reported figures. This leakage rate is considered representative of the hydraulic fracturing industry in the United States generally.

Increases in seismic activity in areas not known for such activity like Pennsylvania and Oklahoma have been recorded following hydraulic fracturing along dormant or previously unknown faults. While the exact explanation for that activity is hard to pin down, it is speculated that it is sometimes caused by the deep-injection disposal of hydraulic fracturing flowback, a by-product of hydraulically fractured wells. Flowback water is fracking fluid that literally “flows back” to the surface during the fracking process. It is a mixture of the original fracking fluid and water from the formation rich in brine (salts) from the targeted reserve formation. If not properly handled, the flowback water may eventually contaminate surface water and water tables close to the surface. In some cases, the flowback water is reintroduced into the formation, and research is ongoing to find

realistic ways to recycle the fluid so that it can be more safely disposed of or even reused in the fracking process. For these reasons, fracking has come under close scrutiny in terms of possible negative ecological consequences. It is already restricted in some countries and banned altogether in others. The EU is drafting regulations that would permit the controlled application of hydraulic fracturing.

13.5 Paints and Surface Coatings

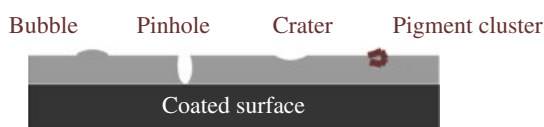
Surface coatings are usually complex multicomponent systems that are required to cover the surface to be protected uniformly and with good resistance to flaking, physical abrasion, and the adverse effects of humidity or other mild chemical interactions. The effectiveness and efficacy with which typical surface coatings, including paints, varnishes, etc., complete their intended purposes depends on several factors, including (i) the chemical nature of the “clean” surface being coated, (ii) the actual cleanliness of the surface at the time of the coating application, and, of course, (iii) the nature and quality of the mixture comprising the applied coating. Since in actual use those factors cannot be controlled completely, coating additives have been used for many years in coating formulations as preemptive solutions to problems that may occur. Their jobs are to help prevent or overcome defects in the coating operation (wetting and spreading or flow), the formation of defects during the drying process (i.e. Gibbs–Marangoni effects due to the presence of oils or dirt on the surface), agglomeration or coalescence of pigments or other particulates in the formulation, the physical strength of the dried coating, and the resistance of the dried coating to humidity (wash ability), among others. Examples of some typical defects are shown Figure 13.16.

Many, if not most, coating defects are related to the interfacial phenomena discussed in previous chapters, especially Chapter 12. It is therefore not surprising that the coating additives used in coatings technology are, in fact, surfactants. The development of coating additives has primarily been driven by market forces, such as better quality, ease of application, speed of drying, etc., all implying the addition of “problem solvers” to the initial formulation of the coating material. If excellent quality and performance are a top priority, then more and better additives will be required. If economy is important, then fewer and/or less expensive (meaning less effective) materials will be the order of the day. In other words, in paints and coatings, as in other areas, you usually get what you pay for.

In the past excellent quality and performance had a very high priority. However, ecological constraints to reduce environmental pollution and possible human contact with potentially harmful chemical species have greatly reduced the number of additives available for the paint and coating formulator to employ. Prime examples are the prohibition of use of lead pigments, the removal of aromatic solvents from the use list, etc. Such changes in the available elements that can be added to formulations have been a constant challenge for additive producers as well as users.

New developments in coating additive technology usually do not lead directly to innovative new developments in paint and coatings. However, they can be important factors in the process of taking a new, innovative coating system from the development lab to market successfully.

Figure 13.16 Representation of some typical coating defects.



13.5.1 Interfaces in Paints and Coatings

Paints and other coatings involve a number of interfaces in their formulation, their application, and their ultimate functioning as applied coatings. Modern formulations usually involve the addition of surfactants and other additives that modify their properties and interactions in each phase of their use in ways that greatly improve their efficiency and effectiveness as tools for enhancing the visual attractiveness of surfaces to which they are applied and to protect and preserve surfaces to which they are applied. Surfactants, because of their nature, can often be used at relatively small concentrations (usually $>1\%$) and are normally listed as “additives” in coating formulation technology. A typical example of an interface in a liquid coating is that between the liquid resin or other solution and solid particles such as pigments, latex particles, and extenders.

An extender or extender pigment is usually a naturally occurring mineral substance, usually white in color, that is added to a paint or coating to improve such properties as durability, cost, and resistance to corrosion or wear. They can also replace a portion of the usually more expensive coloring pigment in a formulation. Some examples of extender pigments are alumina, carbonates, and silicates. Extender pigments are solid particles, meaning a solid–liquid interface, with a wide range of particulate sizes. The solid component of these pigments also makes them effective fillers to increase the volume of a paint with limited binders. This makes the paint more structurally sound and resistant to external wear-causing factors.

A mixture of extenders can often be used to produce a unique degree or form of pigment packing that can be modified to suit several applications. Any additional pigment introduction does not compromise the mechanical durability of the paint. Extender pigments can also provide added benefits based on their chemical properties and how these properties react with a parent paint substance. Some benefits include:

- Increased ease of paint application
- Increased adhesive properties
- Improved film roughness
- Improved paint bulking
- Increased paint film hardness

The wetting and stabilization of the pigment particle dispersion to avoid flocculation are important functions that can be controlled using additives targeting the solid–liquid particle interface. In some situations, foam, primarily incorporated air, is created in the liquid coating during formulation and/or application. The incorporation of air may be facilitated, and air bubbles or foam stabilized somewhat, as a result of the presence of surface-active additives that complete other functions. It is sometimes necessary, therefore, to include defoaming agents, usually silicone derivatives, to remediate the problem (Figure 13.17).

After the application of a coating formulation onto a substrate, other interfaces may become important. The interfacial interactions between the liquid coating film and the solid substrate control, among other properties, the wetting of the substrate, the flow and leveling of the applied material, and the ultimate adhesion of the dried coating to the surface.

Two typical examples of how surface-active additives can successfully overcome coating defects include the use of wetting and dispersing additives for pigment dispersion and stabilization, and the second is concerned with the use of special silicone-based additives to improve substrate wetting. In both cases, the development of new types of additives was important for fulfilling the requirements of the coatings industry.

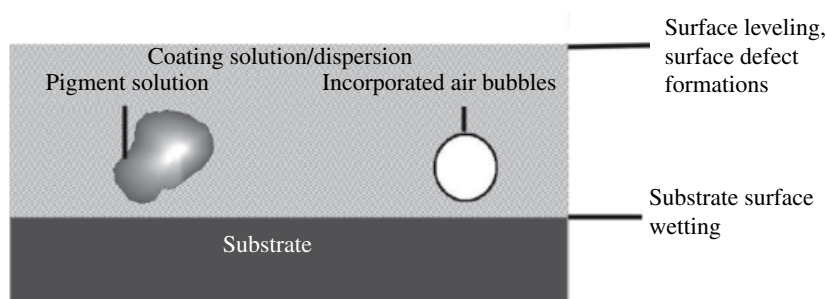


Figure 13.17 Interfaces in a liquid coating material.

13.5.2 Wetting and Dispersing Additives

One of the most important steps in the production of pigmented coatings is the homogeneous distribution of solid pigments within the liquid binder solution or binder emulsion. If the initial pigment grinding step is not optimized, a wide variety of defects can appear both in the formulation itself and in the coating's application and ultimate coating quality. Those defects include:

- 1) Flocculation and agglomeration.
- 2) Decreased gloss due to the formation of irregular dried surface.
- 3) Color inconsistency due to variations in pigment particle size and distribution.
- 4) Flooding/floating, which occurs when coatings containing a variety of pigments exhibit a separation of the pigments due to a nonhomogeneous dispersion.
- 5) Settling in which larger or poorly stabilized pigment particles undergo gravity-induced sedimentation.
- 6) Viscosity instabilities resulting from a nonhomogeneous distribution of pigments, binders, and thickeners.

In the dispersing process, large pigment agglomerates are reduced in size during the grinding phase. Ideally, this leads to the production of primary particles of a desired particle size distribution for the specific formulation. When the pigments agglomerate, particles form clusters in which the interstitial spaces between the individual pigment particles contain air and/or moisture. The individual particles are in contact only along their edges and corners. Interactive forces between the particles are relatively small so and can normally be overcome by traditional dispersing equipment. In the dispersing phase, energy is added to the system, and smaller particles are formed exposing a greater interfacial area of higher energy to the resin solution. Thermodynamics tries to reduce that added energy by reducing the interfacial area. That is, a finely dispersed system is driven to reduce its energy by flocculation. The flocculated formulation will usually exhibit an undesirable and possibly unacceptable loss in color strength, lower gloss, and changes in viscosity that may unfavorably affect application (Figure 13.18).

A number of physical processes take place during pigment grinding that can be divided into the following three steps (Figure 13.19):

Step 1 is wetting, in which the air and adsorbed moisture at the pigment surface is displaced by the resin solution. Any pigment/air interface present is transformed into a pigment/resin

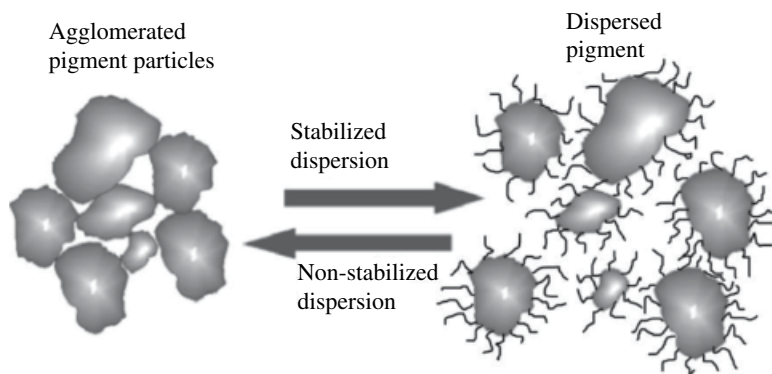


Figure 13.18 Pigment dispersion and flocculation.

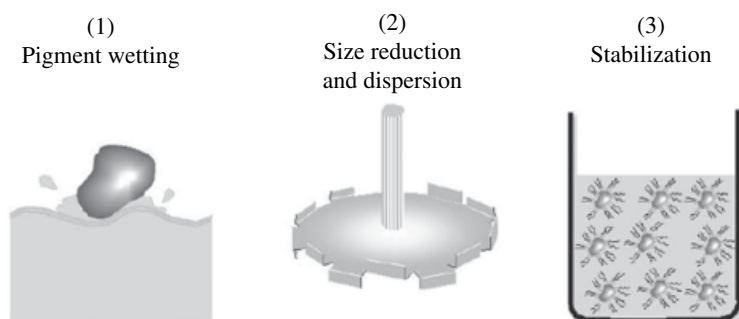


Figure 13.19 Outline of the wetting and dispersing process of pigments.

solution interface. The resin solution must penetrate into the interstitial spaces between the agglomerated particles. In order to facilitate that process, the appropriate surfactant is added as a wetting agent.

Step 2, grinding or particle size reduction, is the heart of the actual pigment dispersion process. In most industrial processes, the application of mechanical energy, either by impact or shear forces, breaks up the agglomerates and reduces particle size. In some cases, the application of sonic agitation can serve as the size reduction mechanism.

Step 3, dispersion stabilization, is achieved by the addition of a surfactant and/or a polymeric stabilizer to prevent flocculation. A number of interfacial mechanisms can be used to try to ensure that the particles remain a sufficient distance apart to prevent flocculation, as pointed out below.

The wetting and stabilization processes (steps 1 and 3) are most affected by the use of surfactants. Wetting agents increase the speed of the wetting process by the binder solution and the displacement of the liquid or gas phases, usually water and air, initially present in the pigment agglomerate. Dispersing agents adsorb on the newly formed “clean” pigment surfaces and improve the stabilization of the pigment dispersion through electrostatic repulsion for ionic surfactants or steric repulsion for nonionic materials. In many cases the same surfactant will act as an efficient wetting and dispersion stabilizing agent.

13.5.3 Wetting Agents

The wetting of pigment agglomerates by the resin solution will be affected by a number of factors. The penetration speed of the liquid into the space between the agglomerated particles can be expressed mathematically, at least to a first approximation, by Eq. (13.1), known as the Washburn or Lucas–Washburn equation. Important factors in the equation include the polarities of the pigment surface and of the binder solution, which will be reflected in the ability of the liquid to wet the pigment surface, the viscosity of the liquid phase, and the geometry of the empty spaces (or pores) within the agglomerate structures. Of special importance is the interfacial tension in the regions where the wetting agent carries out its function – between the pigment surfaces and the resin binder solution:

$$L = (Dt)^{1/2} \quad (13.1)$$

In the equation, L is the distance the liquid will penetrate into a cylindrical pore of radius r in time t . D is a simplified diffusion constant that takes into consideration not only the actual geometry of the theoretical capillary tube representing the space between the particles in the agglomerate but also such physical characteristics of the penetrating liquid as its dynamic viscosity, η , the surface tension of the binder solution, σ , and the contact angle, θ , it makes with the solid surface of the particle. The expanded equation then becomes

$$L = (2\sigma r t \cos \theta / 4\eta)^{1/2} \quad (13.2)$$

Even though in its application to pigment grinding Eq. (13.2) is being applied to anything but an ideal capillary system, the equation has been found to give good results compared to many other systems.

By way of review, wetting agents can be defined as surfactants that reduce the interfacial tension between a liquid and a solid surface and that, as a result, increases the spreading constant, S , so that the wetting process is accelerated (see Eq. (12.8)). As always, the wetting agent can be either ionic or nonionic, depending on the nature of the solid surface to be wet and the overall formulation of the coating formulation. In general, nonionic surfactants tend to be favored as stabilizers mostly because they avoid some of possible unwanted negative effects of charged materials in the final system.

13.5.4 Dispersing Agents

As discussed in Chapter 12, dispersing agents adsorb onto the pigment surface and introduce an electrostatic and/or steric barrier to inhibit the close approach of dispersed particles, thereby helping to avoid unwanted particle flocculation or coalescence. Nonionic dispersing agents that function by steric hindrance often afford two structural features that give them an advantage over the ionic surfactants in systems of pigments dispersed in nonaqueous solvents (Figure 13.20). First, the hydrophilic portions of such surfactants have available several potential points of attachment to the pigment surface for stronger, more resistant adsorption onto the pigment surface. Second, the hydrophobic tails of nonionic surfactants, as for essentially all surfactants, are highly compatible with the hydrocarbon nature of the binder solvent. That compatibility helps ensure that the tails, which supply the steric hindrance to particle approach, can extend to their optimal length into the binder liquid and therefore provide the best protection against flocculation.

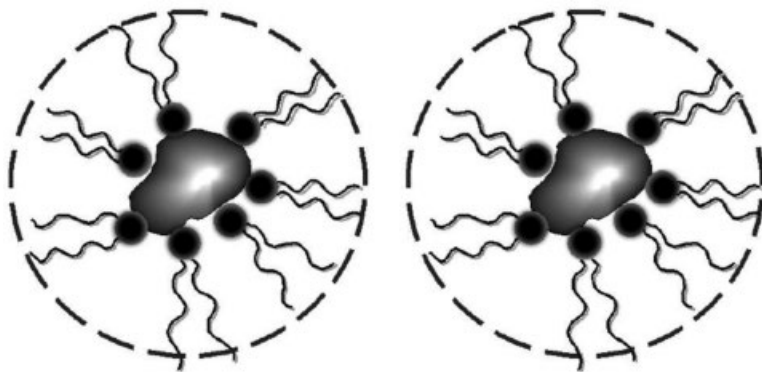


Figure 13.20 Steric stabilization of pigment particles to avoid flocculation.

The structures of classical dispersion stabilizers and wetting agents are such that the hydrophilic head groups will have a significant affinity for the usually polar nature of inorganic pigment and extender surfaces. If the dispersing agent is a polymer, its effectiveness may be enhanced by the interaction of hydrophobic segments of the stabilizer with the resin polymers in such a way that the steric barrier around the pigment particles is extended by “grafting,” so to speak, resin molecules onto the basic steric barrier. Since the resin solvent will usually be organic, it will preferentially associate with the hydrophobic tails or segments of the stabilizer and facilitate the interaction of the hydrophobic binder segments with those of the stabilizer. A strong and stable adsorption is vital to the long-term stability of the dispersion.

Many modern paints and coatings, however, use organic pigments rather than the traditional inorganic types. With organic pigments, the situation with respect to the nature of the adsorption of the additive to the pigment particle is different. Organic pigment crystals are composed of molecules that are basically nonpolar. As a result, the pigments have more nonpolar surfaces and therefore have a less marked attraction for more traditional additives, making it more problematical for them to complete their wetting and stabilization functions. In practice, this means that organic pigments may be less well stabilized against flocculation by traditional wetting and dispersing additives. Organic pigments have gained in popularity primarily because they were able to replace inorganic lead-containing pigments, which are banned in most countries. Because of the weaker adsorption problem, classical LMW wetting and dispersing additives often cannot achieve the necessary stabilization of the organic pigments, especially in uses where the quality of the coating required is very high, such as automotive paints. As a result, new additives have been developed based on high molecular weight polymeric wetting and dispersing additives. Such additives differ from more conventional LMW polymers by having much higher molecular weights similar to the binder materials. In addition, the newer additives usually have a considerably greater relative number of adsorption sites available that provide more adsorption sites on the pigment surface and stronger adsorption. Those structural features result in additives capable of forming durable adsorption layers on many organic pigments.

Maximum stabilization results when dispersant polymer chains are as expanded as possible in the solvent, meaning that they will have significant compatibility with the surrounding resin solution. If this compatibility is reduced, then the polymer chains begin to collapse, reducing the effectiveness of the steric stabilization with a resulting loss in stabilization. The very nature of high molecular weight polymer compatibility in solution, for example, between various coating resins

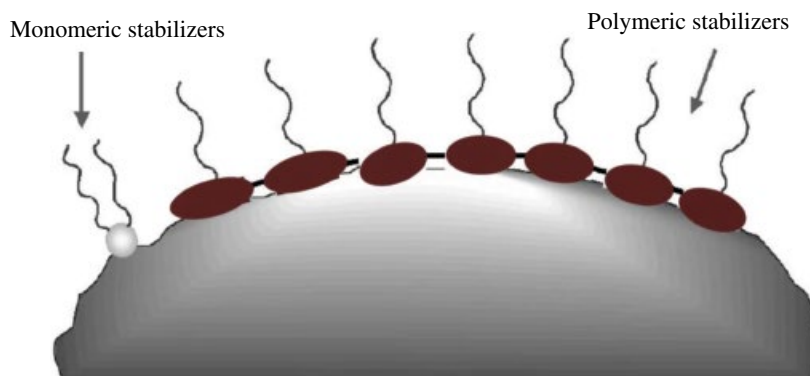


Figure 13.21 Comparison of low molecular weight and high molecular weight (polymeric) wetting and dispersing additives.

and high molecular weight stabilizers, makes chain mixing considerably more restricted than what is seen for LMW additives. As a result, it has become important to develop entire families of chemically related additives (classified according to molecular weight, polarity, and chemical compatibility). Even though the high molecular weight polymeric wetting and dispersing agents were developed primarily for organic pigments, they may also function equally as well with inorganic pigments (Figure 13.21).

In addition to the straightforward question of dispersion stability, another potential defect that can occur in paints and coatings is that referred to as “flooding and floating.” Most pigmented coating systems contain more than one pigment type, which implies differences in surface properties, particle densities, particle sizes, and the like. Flooding and floating occur when the various pigments separate and are no longer homogeneously distributed in the formulation. If local differences in pigment concentrations occur in the coated surface, the defect is referred to as “horizontal” floating. The defect results from what are called Bénard cells, which are approximately hexagonal honeycomb-like structures that form on the drying surface due to convectional flow during solvent evaporation. The Bernard effect is related to, but not identical, to the Marangoni effect, which is related solely to surface tension. When the effect occurs, the dried surface may exhibit a silky or streaked appearance. The painted surface does not have a homogeneous color and appear speckled and/or silky. If the defect does not result from pigment concentration differences in the horizontal paint surface, but there are differences in the vertical direction (through the coating thickness), the phenomenon is called “vertical” flooding. In this case the coating shows a uniform surface color, but the defect becomes noticeable when the “rub-up” test (see below) is utilized. This latter defect is quite common in many paint formulations with more than one pigment, whereas the “horizontal” floating is rarer and may result from uneven heat distribution during the drying process.

In formulations that contain more than one pigment, differences in pigment mobility may be a decisive factor causing a nonhomogeneous pigment distribution. When solvents evaporate from a liquid film, eddies and convection currents may form. Such currents can be attributed to the Gibbs–Marangoni surface effects as well as small differences in temperature, density, and surface tension within the film during drying. When movement occurs in the still-liquid film, the pigments will be carried along, and when differential pigment mobilities occur, pigment separation along with flooding and floating occurs.

Differential pigment mobility can be controlled by using of the appropriate wetting and dispersing agents. If there exists a strong interaction between the polymeric additives and the continuous phase resin solution, the dispersed pigment particles will be tightly associated with the resin system. Pigment mobility will no longer be a “simple” function of particle size and density. With such a strong interaction, the particles will essentially be imbedded in the binder matrix with little opportunity for independent movement relative to neighboring particles. This mechanism can go a long way in preventing defects such as flooding and floating, even when the pigment mixture includes both organic and inorganic pigments that naturally have significantly different particle sizes and densities.

A “quick and easy” test for the presence of differential pigment mobility is the so-called “rub-up” test. After the coating is applied to a surface, but before it completely dries, a small area is lightly rubbed with a finger. In the rubbed area, it is assumed that the pigments have been homogenized by the rubbing action. If the color of the test area exhibits a difference in color from that of an untouched area, then it can be concluded that there is a problem of an unstable pigment mixture. If there is no detectable color difference, then it can be assumed that the mixture is well stabilized.

13.5.5 Surface Wetting with Silicone Surfactants

When applying a coating to a surface, it is vitally important that the liquid coating material complete wet, that is, has a zero contact angle with the solid surface. Otherwise, a smooth, optically, and functionally acceptable finished surface will not be produced once the coating dries.

The concepts of complete wetting and zero contact angle and related principles were introduced in Section 12.7. As pointed out in Chapter 12, the most critical factor controlling solid-liquid wetting phenomena is the interfacial tension and spreading coefficient between the solid and liquid phases. Put most simply, the surface tension or energy of the solid surface to be coated must be higher than the surface tension of the coating liquid as indicated by Eqs. (12.6)–(12.8).

For ideal coating operations, the spreading coefficient of the liquid on the substrate, S (Eq. (12.8)), must be ≥ 0 ; otherwise spontaneous wetting will not occur, and a defective coating can be expected. Other physical factors of the system can also influence results, including a thick coating, where the thickness of the coating layer may help obscure defects, the roughness and porosity of the solid surface may complicate the basic thermodynamics of the interfacial energy relationships involved, and the kinematic viscosity of the coating liquid and the speed with which the coating is applied may introduce turbulence in the liquid during application through the Reynolds number, or the entrainment of air or vapor into the coating due to the Weber number, $We = \rho v^2 l / \sigma$.

Obviously, coating operations can be very complex. In general, coating additives do not lead to new developments in coating operations, but they are usually highly important in the application of new products and techniques. One of the most important of the changes in modern applications is that the markets have gotten away from the use of mineral pigments, especially lead pigments, and turned to organic materials instead. Due to the surface characteristics of organic versus mineral pigments, the stabilization of the new materials required the development of new materials that serve as wetting and dispersing agents. Also leading to new additives has been the switch from solvent-based to aqueous coating systems. Of particular importance are potential problems with the wetting of many surfaces by the aqueous coating dispersion, which is often less than ideal for

the production of a satisfactory finished surface. While conventional silicone additives can do the job, in many circumstances they just do not get the job done so that chemically modified silicone additives have had to step in and do the job.

The limited excursions into the practical applications of emulsifiers, surfactants, stabilizers, wetting agents, and any other name that seems to fit given above just scratch the surface of the underlying field of applications for surface-active materials in our modern lives. No doubt there will be more interesting materials and applications awaiting future investigation.

14

“Multiheaded” Amphiphiles

Gemini and Bolaform Surfactants

The world of chemical structures that exhibit surface activity is quite diverse and is expanding as more synthetic procedures and discoveries of natural materials that fit the definition bring to light more candidates. In addition to the natural surfactants introduced in Chapter 4, there has developed a great deal of interest in molecules containing multiple sites of potential surface activity within a single molecular structure. However, these “newer” structures are not oligomeric or polymeric in nature, but rather covalently bonded and potentially functionally independent surfactants similar to “Siamese twins.” The two classes discussed here include the so-called “gemini” and “bolaform” surfactants.

The first discussion introduces the gemini surfactants that consist of two conventional surfactant molecules chemically bonded together by a “spacer.” The hydrocarbon tails can be short or long, and the polar head groups can be cationic, anionic, or nonionic. The spacer can be short or long and flexible or rigid. Gemini surfactants do not have to be symmetrically disposed about the center of the spacer, although most synthetic pathways tend to make that a convenient characteristic. The gemini surfactants can self-assemble at much lower concentrations than normal surfactants and are usually superior in surface activity compared with conventional materials. Gemini surfactants are very attractive as catalysts, and in most applications involving adsorption, they appear to have several advantages as new synthetic vectors for gene transfection, in analytical separations, in solubilization processes, in nanoscale technology, in biotechnology, in enhanced oil recovery, and as paint and coating additives. So, with all of those touted features, what exactly constitutes a gemini surfactant?

14.1 Two (or More) Can Be Better Than One

Conventional surfactant molecules are composed of one or more long-chain hydrophobic hydrocarbon tails with an ionic or nonionic polar hydrophilic head, as already described. In contrast, the so-called “gemini” surfactants are composed of two hydrophobic tails and two hydrophilic head groups linked by spacer. Figure 14.1 illustrates the basic structure or sequence defining the most gemini surfactants: hydrophobic tail–ionic head group–spacer–ionic head group–hydrophobic tail. The two structures shown are usually symmetrical with respect to the spacer, although that is not an absolute necessity. However, it does seem to make life simpler.

As indicated, the spacer can be attached directly to the identical hydrophilic groups (Figure 14.1a) in which each is bonded to an identical hydrophobic tail. Alternatively, the two identical amphiphilic units may be joined some distance from the head groups along the hydrophobic chain

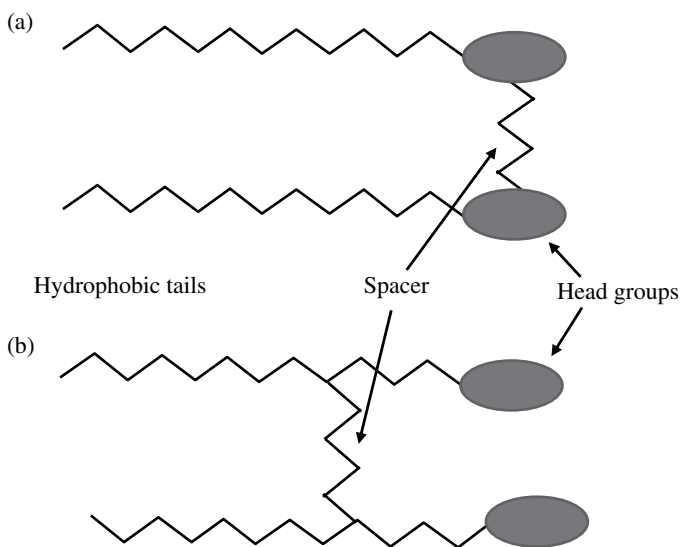


Figure 14.1 The general structure of gemini surfactants with (a) headgroup bound spacer and (b) hydrophobic tail bound spacer.

(Figure 14.1b). The exact structures possibly depend to a great extent on the creativity and skill of the synthetic chemists involved.

In order to simplify somewhat the description of gemini surfactants, especially 2-unit, symmetrical molecules, and to save time and space in writing them, a simple system of three numbers is used. It can be called the “*m-s-m*” nomenclature for lack of a better description. In the system, the “*m*” designates the length of or number of carbon atoms in the hydrophobic chains, and “*s*” gives the number of atoms in the main spacer chain. For example, a gemini surfactant of two conjoined, through the cationic nitrogen, units of dodecyl-*N,N*-dimethylammonium bromide, $\text{C}_{12}\text{H}_{25}\text{N}^+(\text{CH}_3)_2\text{R Br}^-$, where R is the spacer linkage having three methylene groups, would be designated a 12–3–12 gemini surfactant. If the hydrophobic group were changed to C_{16} and the spacer to $-(\text{CH}_2)_6-$, its designation would be 16–6–16.

14.1.1 Structural Characteristics of Gemini Surfactants

From their name, gemini surfactants are like conjoined twins, although in this case the union is intentional and for the most part beneficial. The two units, however, are or could be fully functional if divided. Some important structural features of gemini surfactants can be summarized as follows:

- 1) All gemini surfactants have at least two hydrophobic chains and two hydrophilic head groups.
- 2) Spacer lengths usually range between 2 and 12 methylene or other linking groups, although that is not necessarily a hard and fast rule.
- 3) The spacer groups can be flexible as in the case of methylene groups or more rigid as in the cases of unsaturated or aromatic links such as stilbene. They may also be polar, as in polyethers, or include other heteroatoms such as nitrogen.
- 4) The polar groups will usually be cationic, anionic, or nonionic. Amphoteric or zwitterionic species cannot be ruled out, however.

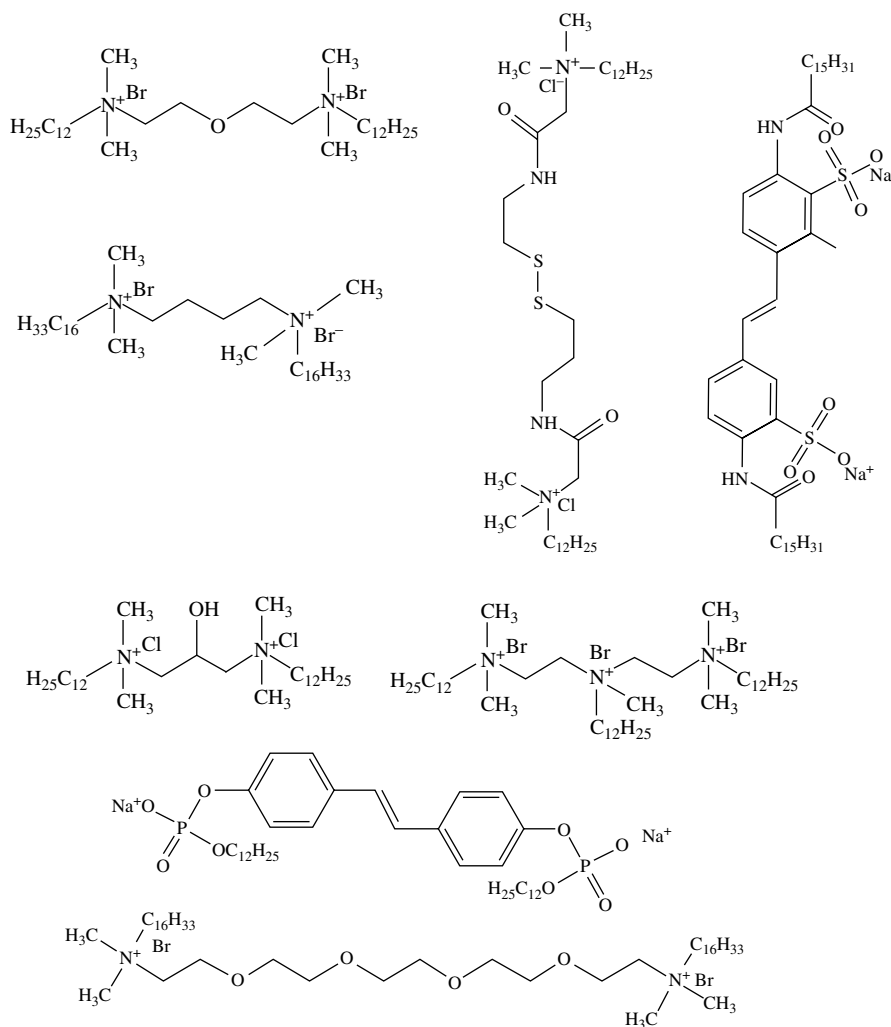


Figure 14.2 Some representative structures of gemini surfactants.

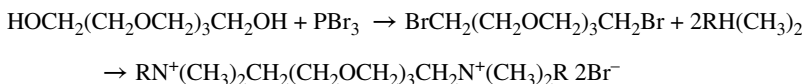
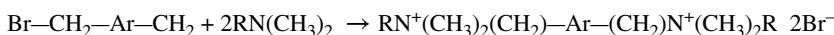
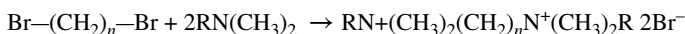
- 5) Symmetrical (identical head groups and hydrophobic tails) and nonsymmetrical (different combinations of one or both elements) gemini surfactants are known, but the symmetrical variety is usually more attainable due to greater synthetic simplicity.
- 6) Gemini surfactants with more than two polar head groups have been reported, which in theory would make them “triad” surfactants.

Some representative structures of this class of surfactants are given in Figure 14.2.

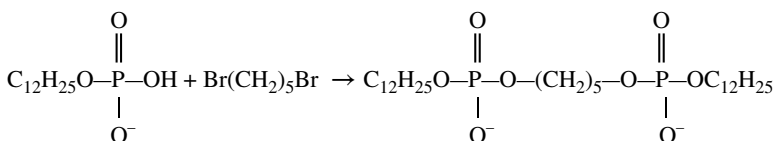
14.1.2 Some Synthetic Pathways to Gemini Structures

The synthesis of gemini surfactants can generally be carried out using reaction schemes familiar to anyone having passed through a first-year organic chemistry course. Of course, a certain level of

Cationic structures (R = long chain alkyl groups, Ar = aromatic groups):

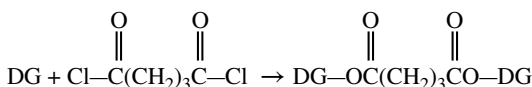


Anionic structures:



(This is actually a more complex, multi-step reaction scheme than illustrated here.)

Nonionic structures (DG = a D-glucose or other glucoside unit):



(This reaction scheme also involves a multi-step reaction process)

Figure 14.3 Some synthetic pathways to gemini surfactant structures.

experience with reagents and manipulation techniques will always be useful. A brief illustration of some of the pathways for the synthesis of representative gemini structures is given in Figure 14.3.

14.1.3 Important Surfactant Properties of Gemini Surfactants

A fundamental property of surfactants that makes them so useful or necessary is their tendency to adsorb at interfaces. They produce interfacial tension reductions because of their split chemical personality. The reasons for this phenomenon have already been discussed in Chapter 3 and will not be repeated here. However, because of the uniqueness of the gemini surfactants and their excellent surface-active properties, some review is warranted.

One of the characteristics of this phenomenon is the surfactant efficiency, pC_{20} , defined as the concentration of a surfactant required to reduce the surface tension of water by 20 mN/m. Gemini surfactants have been shown to have pC_{20} values much lower than their monomeric analogues. The value of pC_{20} for dodecyl trimethylammonium bromide (DTAB) is 2.3 ($\text{C}_{20} = 5.25 \text{ mM}$), while that for the equivalent gemini surfactant with a spacer of two methylene groups is 3.78 ($\text{C}_{20} = 0.16 \text{ mM}$). A higher pC_{20} , of course, means the surface tension reduction by 20 mN/m is reached at lower concentrations. Another important piece of data is the minimum surface tension of water reached at the critical micelle concentration (**cmc**). Gemini surfactants exhibit lower **cmc** values than conventional comparable surfactants. For example, monomeric quaternary ammonium salts have higher **cmcs** than their dimeric analogues. It seems safe to assume that the lower **cmc** values for dimeric and higher oligomeric surfactants are related to the packing efficiency of their hydrophobic tails into a micellar structure. The structure of the hydrophobic group in terms of the number of carbon

atoms in the chain, the presence of unsaturation, branching, etc. also impacts the **cmc**. Up to a point, the same trends in **cmc** are seen in both conventional and gemini surfactants. As the number of carbon atoms in the chain increases, the **cmc** value decreases. As a rule of thumb, the value is halved by the addition of one methylene group to a straight hydrophobic chain. For gemini surfactants, the **cmc** is also affected by the type and the length of the spacer. For short methylene spacers, the **cmc** gradually increases as the number of methylene groups in the spacer increases, up to about four carbon atoms. As more carbons are added, the **cmc** begins to decrease. The current explanation for that effect is that for short spacers, all of the carbons are accommodated at the interface, but as more carbons are added, the spacer becomes more hydrophobic and flexible and begins to pucker or extend out of the aqueous phase or into the micellar structure, thereby pushing the surfactant molecules apart at the micellar surface and producing an increase in the **cmc** value.

Introducing a polar group such as nitrogen or oxygen into the spacer leads to a higher **cmc**, everything else being held constant. For a symmetrical gemini surfactant, say one with a designation of 12-5-12, a **cmc** value of 1.03 mM increased to 1.35 mM with a spacer containing an oxygen atom. The addition of additional oxygen atoms in the spacer exerts a similar effect, that is, an increase of the **cmc**. For gemini surfactant 16-CH₂CH₂OCH₂CH₂-16, the **cmc** is 0.004 mM. The comparable surfactant with three of the oxygen-containing spacer units, 16-CH₂(CH₂OCH₂)₃CH₂-16, the **cmc** increases to 0.02 mM. If the spacer is a more rigid chain containing unsaturation or aromatic groups, the **cmc** also increases for the same hydrophobic and hydrophilic groups.

Not surprisingly, the nature of the head group also affects the micellization of the gemini surfactants. Changing the *N*-methyl groups on the nitrogen of a cationic molecule to *N*-ethyl for a 12-4-12 surfactant decreases the **cmc** from 0.99 to 0.59 mM, as might be expected for making the head group more hydrophobic. However, if the *N*-substituted units are made more hydrophilic, as with the substitution of hydroxyethyl (—CH₂CH₂OH)₂ for ethyl (—CH₂CH₃)₂ groups, the **cmc** decreases.

Another common factor affecting the **cmc** of both normal and gemini surfactants is temperature. The gemini materials, however, tend to part ways with the standard behavior of normal surfactants. For ionic gemini surfactants well below 25 °C, the measured **cmc** will decrease as the temperature is raised, which is not expected, until around 25 °C where it will reach a minimum and then increase with temperature, as one would expect based on normal surfactant behavior. The explanation for that “unusual” behavior is still not entirely clear.

In addition to the self-assembly behavior of gemini surfactants, a number of interesting characteristics related to adsorption behavior that differs from normal surfactants have been noted. The following is a very brief overview of some of the unusual behavior of gemini surfactants at interfaces:

- 1) The area per molecule in a saturated monolayer at the water–air interface involving symmetrical *m*-*s*-*m* gemini surfactants with —(CH₂)_s— spacers exhibit a non-monotonic dependence on *s*. For example, for tail length *m* = 12, the molecular area at the water–air interface is found to increase with *s* for short spacers, reach a maximum at *s* ≈ 10–12, and then decrease for longer spacers. This decrease in the specific area for the *m*-*s*-*m* surfactants is, at first glance, somewhat unexpected given the fact that the molecule becomes physically larger as *s* increases. Based on that criteria it might be expected that there would be a similar parallel increase in the molecular area the molecule would occupy at the interface. A similar series of molecules in which the methylene spacer units are replaced by polar polyoxyethylene spacers, —(OCH₂CH₂)_s—, does, in fact, exhibit such monotonic behavior. Although a complete explanation of that behavior has not been worked out, one can speculate that for the methylene spacers the hydrophobicity and

flexibility of the longer spacer chains allow them to coil up and pucker into the air allowing the head groups to approach more closely and reduce the effective area at the interface. For the polyoxyethylene case, on the other hand, the spacer units are not only more rigid but also hydrophilic and therefore remain more closely associated with the water phase and push the head groups apart, producing a larger surface area per molecule.

- 2) As certain structural and solution conditions, such as the relative sizes of the hydrophobic and hydrophilic groups, temperature, electrolyte concentration, other solutes, etc., are gradually changed, regular surfactants change their aggregate shape usually going from spherical to cylindrical to bilayer structures, that is, in the general direction of decreased curvature of the water–aggregate interface. Gemini surfactants with m - s - m structures, on the other hand, often exhibit a different order of shapes. For example, many 12- s -12 surfactants first form more cylindrical micelles transitioning to spherical and then vesicles as conditions are changed. Gemini surfactants with short spacers may exhibit unusual aggregate morphologies in the form of branched cylindrical micelles, ribbon or thread-like, and ring micelles.
- 3) The length of the spacer, s , also has an effect on other aspects of the phase behavior of gemini surfactant–water mixtures. For molecules of the m - s - m type having $m = 12$, for example, the region of the phase diagram showing hexagonal and lamellar phases decreases with increasing s and disappears when $s \geq 10$ –12 and then reappears when $s \geq 16$. In a ternary single-phase system such as a microemulsion, the phase diagram shows a maximum around $s = 10$.
- 4) Gemini surfactants may also exhibit unusual rheological changes not characteristic of normal surfactants. Dilute solutions of m - s - m surfactants often show a significant increase in viscosity as the concentration of surfactant increases accompanied by evidence of shear thickening. It may be that those effects are related to the unusual aggregate structure transformations observed.
- 5) The alteration of the chemical structure of a substance thereby changing its properties is defined as primary biodegradation, whereas its reduction to carbon dioxide, mineral salts, and biomass is termed ultimate biodegradation. A surfactant is considered easily biodegradable if it is at least 60% biodegraded after 28 days using standard tests. In some comparisons between normal monomeric surfactants and gemini surfactants, it has been found that while the normal single-chain material meets the standard for biodegradability, some of the gemini analogues do not degrade or are much more persistent. One such class that shows that difference includes those gemini surfactants that contain benzene or cyclohexyl rings in the spacer chain. Whereas the monomeric analogues with one phenyl ring are biodegradable, the corresponding gemini surfactants are not. Part of the problem may stem from the excellent bactericidal activity of many gemini surfactants, especially the cationic species. Reducing the spacer length to increase the hydrophilicity of the group does not appear to affect biodegradability significantly, although the presence of sugar-based and amino acid-based hydrophilic groups does seem to help, as does the presence of easily hydrolysable groups such as esters. In general, the degree of biodegradability of a gemini surfactant decreases as the length of the hydrophobic group increases.
- 6) Gemini alkylammonium surfactants exhibit potentially useful bactericidal as well as other biological activity meaning that it is necessary to have good information about the potential toxicity of those materials, especially in terms of aquatic environments. For this purpose, selected model organisms highly sensitive to pollution have been used to determine toxicity. Toxicity is measured as the concentration of surfactant leading to the immobilization of 50% of the test organism in the sample parameter, the IC₅₀. Tests with a series of cationic 12- s -12 surfactants where s was methylene and where s included an oxygen atom (an ether), a nitrogen atom (a diamine), a phenyl ring (for rigidity), and with both bromide and chloride counterions showed

that the overall aquatic toxicity decreased as the hydrophilicity of the surfactant increased. It appears that the structure of the spacer had little or no effect on toxicity. When compared with the monomeric surfactant analogue, the gemini surfactants appear to be less toxic. Similar results have been observed for amino acid-based gemini surfactants.

- 7) Taking into consideration their overall composition, it is not surprising to see that the micellar shapes developed by gemini surfactants take some unusual turns. It has been found that gemini surfactants with short spacers usually produce cylindrical micelles while those with intermediate spacers form mostly spherical micelles and long spacers form mostly vesicles. Other interesting aspects of the self-assembly of gemini surfactants such as aggregation number, the thermodynamics of micelle formation, aggregation phenomena based on molecular geometry, and the like have been studied and reported in the references cited in the bibliography but are too extensive to report here.

14.1.4 Some “Outside the Box” Potential Applications of Gemini Surfactants

Many of the unusual characteristics of gemini surfactants so far reported, when compared with normal surfactants, have led researchers to investigate their potential utility in technological applications not usually contemplated for their monomeric relatives. Those new uses include some very high-tech industrial, pharmaceutical, and biomedical fields that will require a close scrutiny of the stability and safety of the materials. Some of those new fields of interest for gemini surfactants include the following:

- 1) **Nanoparticle technology.** Over the last few decades, nanoparticles, particles of any shape having a diameter of between 1 and 100 nm, have begun to receive increasing attention as uniquely suited tools in many technological areas such as physics, electronics, medicine, and optics, to name a few. The small size and morphology of nanoparticles is responsible for their unique, non-typical physical, and chemical properties. One of their more obvious characteristics is the very high ratio of surface area to bulk material. The interesting and sometimes unexpected properties of nanoparticles are therefore largely due to the large surface area of the material, which dominates the contributions made by the small bulk of the material. Since the interface between the nanoparticle and its surrounding continuous phase is extremely important, the use of surfactants or surface-active polymers immediately becomes of primary interest. While even a highly condensed review of nanoparticle technology is well beyond the scope of this work, it is interesting to give some quick examples of the use of surfactants, especially gemini surfactants, in the nano-world.

Many of the unique characteristics of nanoparticles are controlled or moderated by organic stabilizers, capping and surface ligands, or passivating agents, in other words, by surfactants that act as encapsulating agents, soft templates, or nanocontainers. Gemini surfactants have been shown to be especially useful in the role of surface moderators. An interesting example is the use of a 12–6–12 cationic surfactant as a template for the preparation of hollow metal nanoparticles. Stable gold, silver, and gold–silver alloy nanoparticles have been prepared using the gemini surfactants.

The key to the formation of hollow nanoparticles appears to rely on adjusting the solution conditions so that the gemini surfactant will form vesicles instead of simple micelles during the stage of the synthesis involving the actual deposition of the metal on the surfactant template. The technique has been expanded to include the formation of capsule-like and tubelike nanoparticles, all based on the proper manipulation of the solution characteristics of the gemini

surfactant molecules. The technique allows for the preparation of nanostructures of gold potentially useful for many applications. The use of gemini surfactants reduces the cost of the synthesis of high-quality gold nanoparticles, nanorods in this case, by 90%. Moreover, varying the concentration of the surfactant, the shape of particles can be varied from straight nanorods to rods with bulging ends resembling "dog bones." A number of nanoparticles termed "quantum dots" of lead telluride and cadmium-selenium/zinc sulfide with closely controlled sizes and morphologies have been produced using gemini surfactants.

- 2) **Gene therapy.** Gemini cationic alkylammonium surfactants in particular have been found useful for gene therapy where, as a result of their interactions with DNA, they are useful for introducing genes into cells. In order to operate properly, that interaction must be strong enough to overcome the biological membrane barrier but weak enough to release the DNA in the correct place inside the cell. Some gemini surfactants have been found to bind and package or compact DNA efficiently and form what is called a "genosome" or a "lipoplex." The lipoplex is a combination of a lipid, often a gemini surfactant, and DNA that interact in such a way that the DNA is packaged into a complex that is used to deliver genes through the cell wall membrane. The lipoplex system is a form of nonviral gene therapy since it does not require any components of a virus in order to transport the genetic material. The lipoplex can penetrate the outer membranes of many cell types, presumably through some electrostatic interaction that "opens" the cell wall membrane, so that the genetic material can move into the cytoplasm encapsulated within the endosomes. Release from the endosomes may result from alteration of the aggregation structure of the lipoplex as the pH decreases. Some di-quaternary ammonium gemini surfactants with sugar, peptide, or cholesterol-based groups have been tested as gene "transfection vectors," as have hydroxy ethylated, fluorinated bis-pyridinium, and cysteine-derived gemini surfactants can be also used for this application.
- 3) **Bioimaging.** Bioimaging is a technique in which a stable fluorescent marker or other imaging system is used to highlight certain types of cells or formations *in vivo*. It is a very useful technique for the diagnosis of cancer. Among all of the research results delving into ways for improving the functionality and stability of nanoparticle contrast agents, it has been found that gemini surfactants like 12-2-12 and 12-6-12 can be effective stabilizers in many systems.
- 4) **Drug delivery systems.** Because of their unique surface and colloidal properties as compared with normal surfactants, gemini surfactants have attracted a great deal of attention for potential use in nanoparticle drug delivery systems. Not only are they effective dispersing agents, but also their aggregation characteristics and inherent sensitivity to solution conditions such as pH, temperature, ionic strength, etc. provide a good handle for potential control of the time and place of drug release inside the target organism. The reversible transition from micelles to other structures, especially to vesicles, by changing pH, is very useful, for example, for drug delivery in systems employing gemini surfactants having amino acid hydrophilic groups, where pH is the key driving force to control the aggregation behavior.
- 5) **Solubilization.** Gemini surfactants have been shown to be good solubilization agents for very hydrophobic hydrocarbon and aromatic hydrocarbon materials. Polycyclic aromatic hydrocarbons (PAHs) such as anthracene, naphthalene, fluorene or pyrene, and halogenated aromatics polychlorinated aromatics (i.e. PCBs) are dangerous pollutants that can be removed from aqueous systems using gemini surfactants. Their use in water remediation can significantly reduce the risks to the environment caused by those materials. A number of studies indicate that they are significantly better for solubilization of PAH than their monomeric analogues. Gemini surfactants are also efficient as solubilization agents for many organic dyes used for dyeing textiles, waxes, or oils. Many textile fabrics have a net negative charge, so the use of

cationic surfactants improves the adsorption of solubilized dye on the fiber surface. It appears that the solubilizing power of gemini surfactants increases with increasing hydrophobic chain length and extension of the spacer length, both of which generally lead to larger micelle aggregation numbers.

- 6) **Dispersions.** Another potential application of gemini surfactants due to their ability to form micelles is their capacity to disperse water-insoluble particles and produce stable colloids. Carbon nanotubes have unique electrical, optical, and mechanical properties and are of interest for use in medical sensor technology, electronics, and similar applications. However, the nanotubes are hydrophobic and do not disperse well in water without help. Cationic surfactants, and especially cationic gemini surfactants, show great promise for the preparation of stable carbon nanotube dispersions. Gold and other metal nanoparticle dispersion can also be prepared as described above.
- 7) **Enhanced oil recovery (EOR).** Traditional oil extraction methods usually leave 20–40% of the “available” oil trapped in the porous geological formation due to viscosity and capillary forces, meaning that the actual normal extraction rate is not particularly efficient. The use of modern secondary and tertiary recovery methods, generally termed EOR, greatly improves the level of recovery but requires the use of much more expensive efforts relying to a great extent of the use of chemicals to mobilize the trapped crude. The preferred method usually depends on the physical characteristics of the trapped oil. For so-called heavy and extra heavy crudes, thermal steam flooding is used to reduce the viscosity of the oil and make it more mobile. In the cases of “light” (low viscosity) crude, the choice might be miscible gas flooding. In the case of intermediate and some light crude deposits, chemical flooding is a common choice. Chemical flooding is one of the more successful methods, especially when it includes the use of surfactants. They are added into the flooding liquid to improve the interfacial properties of reservoir fluids, to make them easier to move through the porous formation. In order to “tune” the capillary forces of the trapped oil and to achieve more complete miscibility, the interfacial tension has to be reduced to the lowest possible value. Due to their excellent surface-active properties, cationic gemini surfactants are very effective at lowering surface tension and changing the wettability of the porous rock formation. Comparisons of effectiveness have been carried out with cationic surfactants such as monomeric cetyltrimethylammonium bromide (CTAB, $\text{CH}_3(\text{CH}_2)_{15}\text{N}^+(\text{CH}_3)_3 \text{Br}^-$) and the related 16–2–16 gemini surfactant in model flooding solutions in which *n*-dodecane was used as the oil stand-in and compacted silica gel powder as the porous material. The best results were found when the surfactant concentration used was at the corresponding **cmc**, for CTAB 1 mM and for [16–2–16] 0.018 mM. The gemini surfactant attained a 68% recovery efficiency, while that of the CTAB was 63% even though the CTAB concentration was 56 times higher.

From the limited information presented here, it is obvious that the gemini surfactants, and possibly extended versions of the same theme having three or four surfactant units bound together, present new opportunities for improvements in the use of surfactants in many areas of science and technology, whether well established or completely new and novel.

14.2 Bolaform Surfactants

If you take the idea introduced above for gemini surfactants, that is, link two surfactant molecules together through their hydrophilic head groups or somewhere along the hydrophobic tail and take that link all the way to the end of the tail, you have produced the subject of this section – the

“bolaform” surfactant. Amphiphilic molecules that have hydrophilic groups at both ends of a long hydrophobic hydrocarbon chain have been variously called bolaform surfactants, bola amphiphiles, bolaphiles, or alpha-omega-type surfactants. For simplicity, they will sometimes be referred to simply as “bolaforms.”

The name bolaform comes from a weapon used by South American Indians to hunt rhea (the South American equivalent to the ostrich), guanaco, and other animals and was later adopted by the gauchos to capture cattle. It consists of two or more heavy rocks or balls attached to the ends of one or more thin cords. It was hurled at the feet of the target animal to entangle them and bring them to the ground.

The discussion of gemini surfactants above indicates that such molecular structures, even though they are so similar to normal monomeric surfactants, often exhibit surface-active properties significantly different from their normal counterparts. Compared with single-headed amphiphiles, one might expect that the introduction of a second head group would produce a higher solubility in water, an increase in the **cmc**, and a decrease in aggregation number. That was not the case for the gemini surfactants, so what happens in the case of the bolaform surfactants?

The self-assembly or micellar morphologies of bolaform surfactants include spheres, cylinders, disks, and vesicles. They have also been found to form helical structures, which can then go on to form monolayer microtubular structures. Of the surfactant structures investigated to date, bolaforms seem to bring new and novel characteristics much like their gemini counterparts. Many research papers and reviews have been published in the past few years, especially related to the use of bolaforms for the delivery of bioactive materials, making it an interesting research area for formulators worldwide.

Bolaform surfactants are composed of two or more polar head groups separated by one, two, or three long hydrophobic spacer chains that are usually alkyl chains but can also include unsaturation, cyclic alkyl and aryl groups, fused ring units such as steroids, and heterocyclic rings such as porphyrins. The two hydrophilic groups can be ionic or nonionic, and they can be identical (symmetrical) or different (asymmetrical). The basic structure of bolaforms is illustrated in Figure 14.4.

Bolaform surfactants have been known in nature for some time, one example being tetraether lipids isolated from microorganisms and in particular Archaea cell membranes. Archaea are a domain of single-celled microorganisms similar in many ways to bacteria, in fact once termed “archaebacteria,” which have no nucleus and are “prokaryotes.” However, archaeal cell membranes have some unique characteristics that separate them from bacteria and eukaryote domains (Figure 14.5). Archaea and bacteria are generally similar in terms of their size and shape, although some archaea have flat or almost square shapes not found in bacteria or other microorganisms. Nevertheless, the archaea are in many ways more similar to eukaryotes in terms of their metabolic pathways, enzymes, and enzyme activity. Some major differences from the other domains include the use of ether linkages in their cell lipid membranes rather than the esters used in other organisms, including humans. They are also able to take advantage of a wider range of energy sources including organic compounds such as sugars, hydrogen gas, metal ions, and ammonia. Many

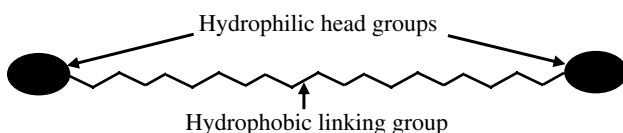
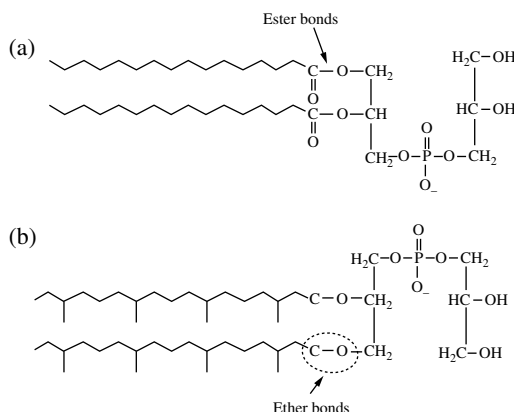


Figure 14.4 An illustration of the basic bolaform surfactant structure.

Figure 14.5 A structural comparison of bolaform surfactants obtained from archaea and bacterial and eukaryotic cell membranes (a) eukaryotic cell membrane lipids with ester bonds linking the hydrophobic and hydrophilic parts of the molecule and (b) archaeal cell membrane lipids with ether bonds linking the two molecular components.



tolerate high salt concentrations well and use sunlight as any energy source and, in some cases, act to fix carbon. It appears, however, that none currently identified can do both. The archaea were originally identified as “extremophiles” since they were usually found in hot springs and salt lakes but are now known to exist in a broader range of more “normal” habitats. They have also been identified as part of the normal human microbiota.

Obviously, archaea are an interesting subject with potential applications in the modern world, but for the current discussion it is the unique character of many of the lipid components of their cells that are of interest, in particular the fact that the membrane lipids involve ether bonds for linking the hydrophobic and hydrophilic groups instead of the ester bonds found in most organisms. Ether bonds are more stable to extreme conditions than the esters, and it is believed that their presence bestows protection for the organism under high stress conditions such as high temperatures, high electrolyte concentrations, and anaerobic conditions. It is also assumed that the role of the molecules is to introduce rigidity and stability in the cell membrane. The fact that many of the archaea lipid molecules are in fact bolaform surfactants peaked the interest of many researchers in areas related to surfactant applications.

One archaea bolaform lipid is composed of two bi-phytanyl chains, basically short isoprene oligomers, which are attached to two glycerol units by ether linkages. In some instances, the unsaturated units will cyclize to cyclopentane rings in the chains. The presence of ether linkages rather than esters as found in other phosphatides and the presence of cyclopentane rings are responsible for the adaptation of the organism to higher growth temperature providing the necessary rigidity and stability and maintaining membrane integrity.

Membranes composed of bolaform surfactants in general are known to be less permeable and more resistant to monolipids. In the absence of other surface-active species, bolaform surfactants self-assemble into monolayer membranes rather than bilayer vesicles encountered for phospholipids.

Bolaforms possess increased aqueous solubility and therefore increased critical aggregation concentration (CAC) in range of 10–10 M much higher in comparison with phospholipids (10 M).

The bolaform surfactants, because of their unique structures, offer various potential advantages in many special applications. Their structures pretty much dictate the possibilities for their aggregation arrangements. Except for special circumstances (see below), bolaforms apparently do not, or cannot, form bilayer membranes, but do form parallel or antiparallel sheets resulting in formation of either unsymmetrical or symmetrical monolayer membranes.

14.3 Chemical Structures and Self-Assembly Patterns

As already noted, bolaform lipids present in the cell membranes of archaea use ether bonds instead of the ester bonds commonly present in lipids synthesized by other organisms. They are more stable under highly acidic conditions and high temperatures, giving the archaea the ability to survive in extreme conditions such as hot sulfurous environments. Since some of the archaea bolaforms have chiral methane groups ($R_1\text{--}_3\text{C--H}$, where each R group is different), they can also form helical structures, which introduce greater rigidity in membranes. The introduction of *cis*-double bonds in their hydrophobic chain, on the other hand, makes bolaforms more flexible or fluid in much the same way that unsaturation in fatty acids and triglycerides lowers their melting point and makes them more fluid.

Bolaform surfactants can be classified in two main categories: symmetric, with same polar head group at each end, and asymmetric, having different head groups at each end. Both classes seem to be capable of forming self-assembled structures with interesting potential applications, especially in the field of nanoscale assemblies.

An interesting aspect of bolaforms is that they can be combined in various ways to produce multilayer membranes and other potentially useful structures. For example, the combination of a symmetrical cationic and a symmetrical anionic–cationic bolaform can be used to produce multilayer membranes. The same can be done with either cationic or anionic bolaforms combined with an anionic or cationic polymer, respectively. Aqueous solutions of bolaform surfactants can be transformed into spherical vesicles by the use of sonication. Short-chain bolaforms form micelles in aqueous solution, while the long-chain molecules produce vesicles. Other unique structures are possible with bolaforms due to their chemical structures, which make them a very interesting class of surfactants for future study and application.

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Index

a

- A-B block copolymer 213
- absorption 17
- N*-acyl-*n*-alkyl taurines 44
- additive-induced micellization 191
- additives
 - dough strengthening 336
 - effect on critical micelle concentration
 - electrolyte effects 146–148
 - organic additive material effects 149–151
 - pH 148–149
 - foaming and antifoaming activity 273–274
 - nature of 194–196
 - polar organic 269
 - wetting and dispersing 361–362
- adenosine triphosphate (ATP) 200
- adhesion 274
- adhesion wetting 309
- adsorption 6, 17, 126, 293–297
 - and adsorbent surface nature 299
 - isotherms 292–293
 - thermodynamics of 97–99
- adsorption at solid–liquid interface 291–292
 - adsorption isotherms 292–293
 - electrical double layer 297–298
 - of surfactant adsorption mechanisms
 - dispersion forces 294–295
 - electrostatic interactions 296–297
 - polarization and dipolar interactions 295–296
- aerating agents 341–342
- aerosols, 45 *see also* liquid aerosols
 - colloidal properties of 282–285
 - sprays 276
- aggregation number 128–129, 132
 - determination of 133
 - elastic light scattering 133
 - electrolyte concentrations effect on 134
 - for surfactants in water 134
 - generalizations 134
 - in nonaqueous solvents 157, 158
 - temperature effect on 134
- agricultural applications, of biosurfactants 89
- alcohol ether sulfate (AES) 37–38
- alcohols 29–30, 69–70
- alcohol sulfates 4, 36
- aliphatic sulfonates 39–40
- alkali metal soaps 3
- alkali soaps 3, 196
 - drawback 23, 64
- alkane sulfates 4
- alkanolamides 54–55
- alkyl aryl sulfonates 4, 40–42
- alkylbenzenes 29, 68–69
- alkylbenzene sulfonates (ABS) 4, 5, 12, 40, 41, 140
- alkyl glucamides 78, 79
- alkyl glyceryl ether sulfonates 46
- alkyl naphthalene sulfonates 3
- alkyl nitrogen compounds 50
- alkylphenols 30, 70
- alkyl polyglucosides 78, 79
- alkyl sulfonate salts 40
- all-block (AB) surfactants 210
- amine oxides 55
- amphipathic structure 96
- amphiphiles
 - expected aggregate characteristics of 172
 - mesophases 166, 242–244

amphiphiles (*cont'd*)
 and polymeric surfactants 205–207
 self-assembly processes 177
 structure, geometric consequences of 173
 amphiphilic fluids
 binary systems, liquid crystalline phases in 166–169
 classical liquid crystals 165–166
 liquid crystalline, bicontinuous, and microemulsion structures 163–165
 phase behavior, temperature and additive effects 170
 amphiphilic interfaces and membranes, curvature of 164–165
 amphiphilic materials 63, 96
 amphiphilic molecules 13
 amphiphilic nature 115
 amphoteric surfactants 13, 20, 55–59, 65, 194
 betaines and sulfobetaines 57–58
 imidazoline derivatives 56–57
 phosphatides 58–59
 anionic food emulsifiers 332–333
 anionic surfactants 13, 19
 carboxylate soaps and detergents 46–48
 economic importance 34
 phosphoric acid esters 48–49
 sulfate esters 35–39
 sulfonic acid salts 39–46
 anisotropic diffusion 167
 antifoaming agents 272–273
 anti-staling agents 336, 338
 aqueous solution, micellar catalysis in 201–203
 association colloids 116
 critical packing parameter 131
 molecular geometry and formation of 130–133

b

bakery products 337–338
 aerating agents 341–342
 anti-staling agents 338
 dough strengtheners 340–341
 starch–emulsifier complexation 339–340
 betaine surfactant 56–57
 bicontinuous aggregate structures 161
 bicontinuous structures 167
 binary mixtures 153
 binary systems, liquid crystalline phases in 166–169
 biodegradability 13
 biodegradation 12
 primary degradation 12
 ultimate degradation 12
 bioimaging 376
 biological implications, of mesophases 176–177
 biological lipids 165
 biological membranes
 membrane surfactants and lipids 177–179
 schematic representation 176
 biomedical applications, of biosurfactants 88–89
 biosurfactants 74, 75
 advantages 82–83
 applications
 agricultural 89
 biomedical 88–89
 cosmetics 89
 detergency and cleaning 89
 food processing industry 89
 metal contamination remediation 88
 microbial-enhanced oil recovery 87–88
 soil washing and bioremediation, of crude oil-contaminated environments 88
 classification 83–84
 critical micelle concentration 81
 disadvantages 83
 examples 84
 exolipids character 80–81
 features 81–82
 functional properties 81
 genetic engineering 91
 high molecular weight species 84
 hydrophile–lipophile balance 81
 limitations 90
 low molecular weight surface-active agents 84
 production/synthesis 80–81
 design and economic evaluation 87
 downstream processing 86
 estimation of biosurfactant activity 87
 factors affecting 85–87
 fermentation and recovery 87
 general environmental factors 85–86
 genetic engineering 86–87

- from inexpensive substrates and waste by-products 85
 - isolation, identification, and purification 87
 - nutritional factors 86
 - reaction/fermentation systems 86
 - research and development 90
 - structures of 76, 77
- block copolymer nonionic surfactants 54
- block copolymers 205
- block-heteric (BH) nonionics 210
- block polymers 226
- bolaform surfactants 13, 377–379
- branched-chain alcohols 30, 70
- butter 344–345
- C**
- carboxylate soaps 23–24, 64–65
 - and detergents 46–48
- carboxylic acid soaps 34
- carboxymethylcellulose (CMC) 208, 220
- cationic surfactants 13, 19, 49–51
 - applications 49
 - categories 50
 - economic importance 51
 - heterocyclic cationic surfactant structures 50
 - nitrogen-based 107
- cetyltrimethylammonium bromide (CTAB) 49
- cheeses and cheese substitutes 344
- chemical industry applications 6
- chocolate coatings 336
- cis*-unsaturated fatty acid chains 340
- cleaning process 314–315
- cloud point 13, 118, 152, 153
- cmc *see* critical micelle concentration (cmc)
- coalescence 13
- cocoa butter substitutes (CBS) 336
- coffee creamers 349
- coffee whiteners 348–349
- cohesion 274
- colloidal properties of aerosols 282–285
- colloidal stability 227
- colloids 14
- comb copolymers 205
- comb polymers 226
- condensation, aerosol formation by 279–282
- condensed film 232
- contact angle 14
- cosmetics and personal care products 6
- cosmetics industry applications, of
 - biosurfactants 89
- co-surfactants 182–184
 - in microemulsions 122
- counterions 14
- critical aggregation concentration (cac) 215, 379
- critical micelle concentration (cmc) 14, 118, 128–130, 135, 188, 191–193, 197, 198, 200, 222, 223, 238, 240, 249, 250, 265, 266, 269, 270, 272, 313, 317–319, 353, 372–373
 - additives effect on 146
 - electrolyte effects 146–148
 - organic additive material effects 149–151
 - pH 148–149
 - determination of 135
 - hydrogen substitution effect 143
 - hydrophilic groups 143–145
 - cationic head groups 146
 - counter ion 146
 - electrolyte effects 145
 - location on hydrophobic chain 144
 - nonionic head groups 143
 - hydrophobic groups 135, 138, 139
 - aromatic rings 139, 141
 - chain branching 135
 - chain length 135
 - ethylenic unsaturation effects 141
 - fluorinated hydrocarbons 142
 - fluorinated surfactants 143
 - nonionic surfactants 137
 - polar substitution 141
 - siloxanes 142
 - in mixed surfactant systems 153–154
 - in nonaqueous media 154
 - nonpolar solvents 155–159
 - polar organic solvents 155
 - of sodium alkyl sulfates 138, 139
 - in organic media 157
 - of sodium alkylbenzene sulfonate surfactants 139, 140
 - of sodium alkyl sulfonate surfactants 139, 140
 - temperature effect on 151–152
- critical packing parameter 131
- crumb softeners 337

crystallization 121
 crystal stabilizer 336
 cubosomes 121, 167

d

dairy and nondairy substitutes, emulsifiers in
 butter and margarine 344–345
 cheeses and cheese substitutes 344
 coffee whiteners 348–349
 dairy drinks 347
 deserts and yogurts 344
 ice cream 347–348
 milk 343
 whipped cream and nondairy whipped
 toppings 345–347
 dairy drinks 347
 deserts 344
 detergency 14, 314
 and cleaning, biosurfactant
 application 89
 and soil removal 314
 detergent-class olefins 68
 detergents 8
 and cleaning products 5
 diacetyltartaric acid esters of monoglycerides
 (DATEM) 47–48
 dialkyl sulfosuccinates 139
 diffusion coefficient 283
N,N-dimethyl-3-aminopropane-1-sulfonic
 acid 65
 dimethyl siloxanes 72
 disjoining pressure 262
 dispersing agents 363–366
 dispersion forces 14
 dispersions 14, 321–322, 377
n-dodecane 22–25, 63–65
 dodecane sulfuric acid ester 64
 dodecanoic acid 64
 dodecylbenzene 42
 dodecyl polyoxyethylene (POE)
 polyether 64
 dodecyl trimethylammonium chloride 65
 double-ended surfactants 268
 dough strengtheners 340–341
 dough strengthening additives 336
 drug delivery systems 376
 dye solubilization 135, 150, 155

e

elastic/crumb modulus 338
 electrical double layer 297–298
 electrolytes 198–199
 emulsification 6
 emulsifiers/emulsifying agents 14
 as crystal modifiers 335–337
 emulsion polymerization 223–224
 emulsions 14, 122
 liquid–liquid interface 226–227
 vs. microemulsions 180
 mixed surfactant systems and interfacial
 complexes 239–242
 multiple
 nomenclature for 254
 preparation and stability of 254–255
 primary emulsion breakdown, pathways for
 255–256
 surfactants and phase components
 256–258
 stability 227–230
 amphiphile mesophases and 242–244
 lifetimes of 230–232
 surface activity and 235–239
 surfactant structure and 245–254
 theories of 232–233
 type and surfactant nature 233–235
 enhanced oil recovery (EOR) 356–358, 377
 ethoxylated sorbitan esters 78, 355
 ethylbenzene, solubilization of 192
 expected aggregate characteristics vs. surfactant
 critical packing parameter 131
 extremophiles 379

f

fatty acids 14, 27, 67
 fatty alcohols 14
 fatty alcohol sulfates 36
 feathering 349
 flocculation 14, 228
 flooding and floating 365
 flotation 6
 fluorinated poly-siloxanes 212
 fluorinated surfactants 143
 fluorine-substituted carbon chains 212
 fluorocarbon compounds 71–72
 fluorocarbon surfactants 31–32, 70, 142

fluorosurfactant hydrophobic groups 71
 foam boosters 14
 foam breakers 271
 foams 6, 225
 chemical structures of antifoaming agents 272–273
 foaming and antifoaming activity of additives 273–274
 foam inhibition 271–272
 foam inhibitors 14, 271
 physical basis for formation 260–263
 spreading coefficient 274–276
 surfactants role in 263–266
 amphiphilic mesophases and foam stability 268–269
 foam formation and surfactant structure 266–268
 foaming properties, additives effect on 269–271
 food processing industrial application, of biosurfactants 89
 foods and food packaging 6
 fracking fluid 358

g

gemini alkylammonium surfactants 374
 gemini surfactants 14, 21
 applications 375–377
 properties of 372–375
 structural characteristics 370–371
 synthetic pathways 371–372
 generic alkylene oxide molecule 209
 gene therapy 376
 genetic engineering 86–87, 91
 genosome 376
 Gibbs equation 98, 108, 110, 182, 226, 227, 238
 gluten 338
 glycerol monostearate (GMS) 325
 graft copolymers 205
 gums 207–208

h

hard water, components of 64
 Hartley micelles model 125–127
 head groups (surfactant) 14, 18, 19
 hemimicelles 214

heteric-block (HB) nonionics 210
 heterocyclic cationic surfactants 50
 heteropolymers 205
 hexagonal close packed phase 120
 hexagonal liquid crystal 122
 homopolar diamond lattice 288, 289
 homopolar solids 289
 homopolymers 205
 horizontal floating 365
 hydraulic fracturing/fracking 358–359
 hydrogen bonding 14
 hydrogen-terminated fluoroalcohols 71
 hydrophile 63
 hydrophile–lipophile balance (HLB) 14, 81, 164, 245–250
 hydrophilic 15
 hydrophilic effect 156
 hydrophilic groups 21, 61, 143–145, 148
 hydrophobes 63
 hydrophobic effect 156
 hydrophobic groups 20, 61, 65, 135–143
 alcohols 69–70
 alkylbenzenes 68–69
 alkylphenols 70
 basic structure 61, 62
 evolutionary pathways 66
 fluorocarbons 70–72
 natural fatty acids 67
 nature of 61
 olefins 67–68
 paraffins/saturated hydrocarbons 67
 polyoxypropylene 70
 hydrophobic materials 15
 hydrophobic patches 340
 hydrotropes 199–201

i

ice cream 347–348
 imidazoline-derived surfactants 56–57
 industrial sorbitol 77
 inorganic electrolytes 269
 interfaces
 and adsorption 97–99
 atoms (molecules) at 95–97
 definition 15, 93, 94
 orientation of surfactant molecules at 96
 in paints and surface coatings 360–361

interfacial energy 94
 reduction, modes of surfactant action for 116
 interfacial tension 15, 95
 and surface tension 99–101
 ion binding 134, 145
 ionic crystal lattice 288
 ionic polymers and proteins 219–222
 ionic solids 288–289
 ionic surfactants
 Krafft temperature of 118, 119
 microemulsions 183–184
 temperature/solubility relationship for 118
 ion pairing 145
 isotropic diffusion 167

k

Kelvin equation 102
 kerosene 67
 Klevens constant 136
 Klevens equation 136
 Krafft temperature 107, 117, 138
 of ionic surfactants 118, 119

l

α -lactalbumin 343
 β -lactoglobulin 343
 lamellar film 262
 lamellar liquid crystal 121–122
 lamellar phases 120
 Langmuir (L class) isotherm 292
 lauric acid 64
 lauric fats 347
 lauryl alcohols 30, 69
N-lauryl sarcoside 47
 leather and fur processing 6
 lecithin surfactants 58–59, 76, 333–334
 lignin sulfonates 46
 linear alcohols 69
 linear alkylbenzene sulfonates (LABS) 5, 12,
 39–41
 linear alkyl sulfates (LAS) 30
 linear secondary alkyl sulfates 12
 lipopeptide biosurfactants 89
 lipophilic 15
 lipophobic 15
 lipoplex 376

liposomes *see* vesicles
 liquid aerosols
 colloidal properties 282–285
 condensation 279–282
 mist and fog formation 276–277
 nozzle atomization 277–278
 rotary atomization 278–279
 spraying techniques 276–277
 liquid crystalline structures, surfactant molecules
 arrangement 120
 liquid crystals 168
 classical 165–166
 cubic phase 121
 hexagonal phase 121
 thermotropic 121
 liquid–liquid interface 226–227
 liquid soil removal 317–318
 liquid vs. solid surfaces 290–291
 London forces 15
 lyophilic 15
 lyophobic 15
 lyotropic liquid crystals 121
 lyotropic phase 122
 lyotropic self-assembly 163–164
 lysolecithin 58

m

macromolecular emulsifiers 229
 macromolecular materials 269
 margaric acid 344
 margarine 344–345
 maximum additive concentrations (MAC)
 194, 195
 maximum extended (hydrocarbonchain)
 length 132
 medicine and biochemical research 6
 membrane lipids and surfactants 177–179
 mesophases
 of amphiphiles 166
 biological implications of 176–177
 theoretical analyses of 171
 metal contamination remediation 88
 metallic lattice 288, 289
 metallic solids 289
 metal processing 6
 metastable foams 261

- methyl cellulose (MC) 218
- micellar catalysis
 - in aqueous solution 201–203
 - in nonaqueous solvents 203
- micellar core volume 131
- micellar solubilization
 - defined 188
 - in surfactants micelles
 - added electrolytes effect 198–199
 - geography 189–191
 - hydrotropes 199–201
 - nature of additives 194–196
 - nonelectrolyte solutes effect 197–198
 - pH and pressure effects 199
 - structure and solubilization process 191–194
 - temperature effect 196–197
- micellar theory, history and development of 123–130
- micelles 15, 116, 118
 - aggregation number 132
 - charge on 130
 - formation 6, 119
 - classical theories of 128–129
 - entropy-driven process 130
 - free energy 129
 - in mixed surfactant systems 153–154
 - in nonaqueous media 154–159
 - manifestations of 124–127
 - mass action model 128–129
 - phase separation model 129
 - Hartley model 125–127
 - in nonpolar solvents 155–159
 - vs. microemulsions 180–181
 - shapes of 125
 - solubilization in 189–191
 - thermodynamics of 127
- micellization 125, 126
 - additives effect on
 - electrolyte effects 147–148
 - organic additive material effects 149–151
 - pH 148–149
 - temperature effects 151–152
 - counterion effects on 145–146
 - enthalpy of 130
 - free energy of 129–130
 - in mixed surfactant systems 153–154
 - in nonaqueous media 154–159
 - organic additive material effects 149–151
 - temperature effect on 151–152
- microbial-enhanced oil recovery (MEOR) 87–88
- microemulsions 122, 161, 179
 - vs. emulsions 180
 - immiscible liquid phases 183
 - ionic surfactant systems 183–184
 - vs. micelles 180–181
 - nonionic surfactant systems 184–185
 - O/W microemulsions 183, 184
 - in petroleum industry 185
 - in tertiary oil recovery 185
 - W/O microemulsions 183, 184
- milk 343
- mining and flotation 6
- mist and fog formation 276–277
- mixed heteric-block (MHB) materials 210
- mixed surfactant systems and interfacial complexes 239–242
- molecular lattice 288, 289
- molecular solids 289
- monoglycerides 326–327
- monoglycerides, derivatives of 327–329
- 1-monolinolein 340
- monomolecular film 232
- 1-monoolein 340
- 1-monopalmitin 340
- 1-monostearin 340
- multiheaded amphiphiles
 - bolaform surfactants 377–379
 - chemical structures and self-assembly patterns 380
 - gemini surfactants
 - applications 375–377
 - properties 372–375
 - structural characteristics 370–371
 - synthetic pathways 371–372
- multilayer vesicles 173
- multiple emulsions
 - nomenclature 254
 - preparation and stability 254–255
 - primary emulsion breakdown pathways 255–256
 - surfactants and phase components 256–258

n

nanoparticle technology 375–376
 natural cellulosic materials 207–208
 natural fatty acids 27, 67
 natural surface-active compounds 76
 natural surfactants 74–77
 natural yogurt 344
 nitrogen-based cationic surfactants 107
 nonaqueous cleaning solutions 320–321
 nonaqueous solvents, micellar catalysis in 203
 nondairy whipped toppings 345–347
 nonelectrolyte solutes 197–198
 non-hydrocarbon-based hydrophobic group 72
 nonionic polymers 218–219
 nonionic surfactants 15, 20, 137, 202
 adsorption efficiency 107
 alkanolamides 54–55
 amine oxides 55
 block copolymer 54
 microemulsions 184–185
 polyglycerols and polyols, derivatives of 52–54
 polyoxyethylene-based surfactants 51–52
 nonpolar, hydrophobic surfaces 299–300
 nonylphenol–POE nonionic surfactants 222
 nozzle atomization 277–278

o

oilfield chemicals 6
 oil-in-oil (O/O) emulsions 225, 226
 oil in water (O/W) emulsions 225
 oil in water (O/W) microemulsions 183, 184
 olefins 28, 67–68
 α -olefins 28
 α -olefin sulfonates 40
 oleochemicals 15
 oleomargarine 345
 organically modified poly-siloxanes 73
 organophosphorus surfactants 49
 oriented wedge theory 234
 Ostwald ripening 231

p

paints and surface coatings 359
 dispersing agents 363–366
 interfaces in 360–361
 surface wetting with silicone surfactants 366–367

wetting
 agents 363
 and dispersing additives 361–362
 paints, lacquers and coatings 6
 paper and cellulose products 6
 paraffins 28, 67
 paraffin sulfonates 39
 pentosans 338
 perfluoroalkyl sulfonates 40
 petroleum and natural gas extraction 355–356
 enhanced oil recovery 356–358
 hydraulic fracturing/fracking 358–359
 petroleum sulfonates 40
 pharmaceuticals 6
 phase diagrams 122, 171
 phase inversion temperature (PIT) 250–251
 phosphatidyl surfactants 58–59
 phosphoric acid esters 48–49
 plant protection and pest control 6
 plastics and composite materials 6
 plateau borders 262
 Pluronic 30–31, 355
 polar organic additives 269
 polar organic solvents, aggregation in 155
 polar, uncharged surfaces 300
 poloxamers 211, 355
 polyacrylamide 208
 polyacrylate 219
 polyacrylic acid 208
 polyelectrolytes 206, 219
 polyether-modified siloxanes 74
 polyethylene oxide (PEO) 73, 218
 polyglucosides 78, 79
 polyglycerol esters 331
 polyglycerol polyricinoleates 53
 polyglycidyl addition products, isomers of 53
 polyhydric emulsifiers 330
 polymeric biosurfactants 212
 polymeric nonionic surfactants 211
 polymeric surfactants
 and amphiphiles 205–207
 in emulsion polymerization 223–224
 interactions with polymers 214–215
 ionic polymers and proteins 219–222
 nonionic polymers 218–219
 surfactant–polymer complex formation 215–218
 at interfaces 213–214

natural cellulosic materials, gums, and proteins
 modification 207–208
 and solubilization 222–223
 synthetic 208–212
 polymerized vesicles 174–175
 polymers
 chemical structures of 206–207
 general classes of 206
 polymethacrylate 219
 polyol surfactants 52–54
 polyoxyethylene (POE)-based surfactants
 51–52
 polyoxyethylene (POE) nonionic surfactants
 107, 110, 152, 169
 polyoxypropylene (POP) 142
 polyoxypropylene–polyoxyethylene (POP-POE)
 block copolymers 211
 polyoxypropylenes (PO) 30–31, 70
 polypropylene glycol (PPG) 218
 polypropylene oxide 73
 poly-siloxanes 212
 polyvinyl acetate (PVAc) 218
 polyvinyl alcohol (PVA) 218
 polyvinylpyrrolidone (PVP) 218
 positive spreading coefficient 275
 potassium thiocyanate (KCNS) 228
 pre-micellar aggregates 191
 processed cheeses 344
 proppants 358
 propylene tetramer (PT) 4
 propylene tetramer (PT)-benzenesulfonates 4, 5
 protein emulsifiers 349–351
 as emulsifying agents 352–353
 as foam stabilizers 351–352
 protein–low molecular weight emulsifier
 interactions 353–354
 proteins 207–208
Pseudomonas aeruginosa 81, 84

r

random copolymers 205
 reverse hexagonal close packed phase 120
 rewetting characteristics 287
 Reynolds number 283
 rhamnolipids 81, 84, 85, 88, 90
 ricinoleic acid 53
 rodlike micelles 171
 rotary atomization 278–279

s

salting-in agents 253
 salting-out additives 253
 saponins 76
 saturated fatty acid 339
 saturated hydrocarbons 28, 67
 SDS *see* sodium dodecyl sulfate (SDS)
 secondary *n*-alkyl sulfonates 39
 secondary olefin sulfates 4
 self-assembled colloids 116
 self-assembly 15
 silicone-based surfactants 72–74, 142
 silicone surfactants 32
 siloxane oligomers 72
 single bilayer vesicles 173
 soaps 3, 8, 11, 15, 23–24, 34, 46–47, 64, 67,
 117, 121
 soap stock 85
 sodium alkylbenzene sulfonate surfactants
 139, 140
 sodium alkyl sulfates 138, 139
 sodium alkyl sulfonate surfactants 139, 140
 sodium chloride 288
 sodium di-2-ethylhexyl ester 44
 sodium dodecyl sulfate (SDS) 2, 23, 26, 64, 66
 sodium heptadecafluoro octane sulfonate 70
 sodium lauryl sulfate 26, 66
 sodium stearyl-2-lactylate (SSL) 47
 sodium sulfonate surfactants 106
 soil re-deposition 318
 soil types 315–316
 soil washing and bioremediation, of crude
 oil-contaminated environments 88
 solid foams 261
 solid soil removal 316–317
 solid surfaces
 adsorption at solid–liquid interface 291–292
 adsorption isotherms 292–293
 electrical double layer 297–298
 mechanisms of surfactant adsorption
 293–297
 vs. liquid surfaces 290–291
 nature of 287–290
 surfactant adsorption 307–308
 surfactant adsorption mechanics 298–299
 adsorption and nature of adsorbent
 surface 299
 nonpolar, hydrophobic surfaces 299–300

- solid surfaces (*cont'd*)
 - polar, uncharged surfaces 300
 - surfaces having discrete electrical charges 301–302
 - surfactant structure and adsorption from solution
 - adsorption by uncharged, polar surfaces 306
 - surfaces possessing strong charge sites 303–306
 - surfactants at nonpolar, hydrophobic surfaces 306–307
 - suspensions and dispersions 321–322
 - wetting and related phenomena 308–311
 - cleaning process 314–315
 - detergency and soil removal 314
 - liquid soil removal 317–318
 - nonaqueous cleaning solutions 320–321
 - soil re-deposition 318
 - soil types 315–316
 - solid soil removal 316–317
 - surfactant manipulation 311–314
 - surfactant structure and detergency, correlations of 319–320
 - wetting control by surfactants 314
- solubilization 16, 376–377
 - defined 188
 - in surfactants micelles
 - added electrolytes effect 198–199
 - geography 189–191
 - hydrotropes 199–201
 - nature of additive 194–196
 - nonelectrolyte solutes effect 197–198
 - pH and pressure effects 199
 - structure and process 191–194
 - temperature effect 196–197
- sophorolipids 85
- sorbitan esters 54, 77, 78, 355
- sorbitan monostearate 325
- sorbitan tristearate 325–326
- sorbitol derivatives 329–330
- spacer chain 16
- spontaneous emulsification 356
- spray-dried nondairy whipped toppings 349
- spreading coefficient 274–276
- spreading process 309, 310
- spring model of membranes 164, 165
- stability, emulsions 227–230
 - amphiphile mesophases and 242–244
 - lifetimes of 230–232
 - surface activity and 235–239
 - surfactant structure and 245–254
 - theories of 232–233
- staling 338
- starch–emulsifier complexation 339–340
- stearic acid crystals 289
- sticking coefficient 100
- Stokes equation 283
- sucrose esters 78, 79, 331–332
- sulfated alkanolamides 37
- sulfated alkylphenol ethoxylates 38
- sulfated ethers 37–38
- sulfated fats and oils 38–39
- sulfated fatty acid condensation products 36–37
- sulfated monoesters of ethylene glycol 37
- sulfated monoglycerides 37
- sulfate esters
 - fatty alcohol sulfates 36
 - sulfated fatty acid condensation products 36–37
 - synthesis 35–36
- sulfobetaines 56–57
- α -sulfocarboxylic acids 42–43
- sulfo-esters and amides 43–46
- sulfonated castor oil 3
- sulfonic acid salts
 - aliphatic sulfonates 39–40
 - alkyl aryl sulfonates 40–42
 - alkyl glyceryl ether sulfonates 46
 - lignin sulfonates 46
 - α -sulfocarboxylic acids 42–43
 - sulfo-esters and amides 43–46
- sulfosuccinamates 45
- sulfosuccinate esters 44
- sulfosuccinimides 45
- surface-active agent 16
- surface-active molecule structure 18
- surface activity 1, 17, 71, 225
 - emulsion stability 235–239
- surface area 131
- surface energy
 - free energy 290
 - reduction, modes of surfactant action for 116
- surface tension 16, 291
 - defined 99
 - effect of added alcohols 102, 104

- electrolytes effects on 102, 103
- of liquid/high-energy solid 94–95
- at liquid–vapor interface 95
- of solutions 102–103
- reduction and surfactants 103–105
- surface curvature effect 101–102
- surfactant structure, efficiency and effectiveness 105–113
- temperature coefficient of 101
- variation in liquid mixtures 102, 103
- surface wetting with silicone surfactants 366–367
- surfactant adsorption
 - mechanics of 298–299
 - nature of adsorbent surface 299
 - nonpolar, hydrophobic surfaces 299–300
 - polar, uncharged surfaces 300
 - surfaces having discrete electrical charges 301–302
 - mechanisms of 293–297
- surfactant efficiency 372
- surfactant/nonpolar solvent systems 190
- surfactant phase information 161–163
- surfactant–polymer complex formation 215–218
- surfactant–polymer interactions 223–224
- surfactants 16
 - adsorption at interface 105–113
 - amphoteric 20, 55–59
 - anionic 19
 - applications 5–7
 - in bakery products 337–338
 - aerating agents 341–342
 - anti-staling agents 338
 - dough strengtheners 340–341
 - starch–emulsifier complexation 339–340
 - based on natural sugar-based polar head groups 78–79
 - cationic 19, 49–51
 - characteristics 7
 - classes, characteristics of 61, 62
 - classification 19–21
 - classification of 33–34
 - commercial markets for 10
 - economic considerations 61–62
 - economics of 8–10
 - emulsifiers as crystal modifiers 335–337
 - emulsifier use in dairy and nondairy substitutes
 - butter and margarine 344–345
 - cheeses and cheese substitutes 344
 - coffee whiteners 348–349
 - dairy drinks 347
 - deserts and yogurts 344
 - ice cream 347–348
 - milk 343
 - whipped cream and nondairy whipped toppings 345–347
- emulsion type and nature of 233–235
- enhanced packing efficiency 182
- in the environment 11–13
- family tree 63–65
- in food emulsifiers, chemical structures
 - anionic food emulsifiers 332–333
 - lecithin 333–334
 - monoglyceride derivatives 327–329
 - monoglycerides 326–327
 - polyglycerol esters 331
 - polyhydric emulsifiers 330
 - sorbitol derivatives 329–330
 - sucrose esters 331–332
- hydrophilic groups 21, 26
- hydrophobic groups 20, 26, 27, 29, 135–143
- legal status 324
- mesophases, in aqueous solution 117
- miscellaneous biological structures 32, 33
- mixed systems and interfacial complexes 239–242
- nonionic 20, 51–55
- paints and surface coatings 359
 - dispersing agents 363–366
 - interfaces in 360–361
 - surface wetting with silicone surfactants 366–367
 - wetting agents 363
 - wetting and dispersing additives 361–362
- petroleum and natural gas extraction 355–356
 - enhanced oil recovery 356–358
 - hydraulic fracturing/fracking 358–359
- pharmaceutical and medicinal applications 354–355
- phase behavior, temperature and additive effects 170
- phase spectrum in solution 119–123
- protein emulsifiers 349–351
 - as emulsifying agents 352–353

surfactants (*cont'd*)

- as foam stabilizers 351–352
 - protein–low molecular weight emulsifier interactions 353–354
 - selection of 21, 62
 - solubility of 116–119
 - solubilizing groups 19–21, 25
 - structure and adsorption from solution
 - adsorption by uncharged, polar surfaces 306
 - surfaces possessing strong charge sites 303–306
 - surfactants at nonpolar, hydrophobic surfaces 306–307
 - structure and detergency, correlations of 319–320
 - structure and emulsion stability
 - application of HLB and PIT 251–253
 - effective HLB, additives effect on 253–254
 - hydrophile–lipophile balance 245–250
 - phase inversion temperature 250–251
 - structure, geometric consequences of 132
 - sulfated fats and oils 38–39
 - sulfonic acid salts 39–46
 - and surface tension 105–113
 - temperature effect on 134
 - typical food emulsifier sources 324–326
 - wetting process, manipulation of 311–314
 - zwitterionic 20
- surfactant tail 16
- suspensions 321–322
- synthetic polymeric surfactants 208–212

t

- tail groups 18
- tallow alcohols 30, 69
- taurine derivatives 4
- α -tending emulsifiers 347
- tetrapropylene ($C_{12}H_{24}$) 28, 67–68
- textiles and fibers 6
- thermotropic liquid crystals 121
- transfection vectors 376
- trans*-unsaturated fatty acids 340
- tridecyl benzene 42
- triglyceride crystals 335
- Tween 20 (polyoxyethylene (20) sorbitan monolaurate) 246–247

u

- ultra-high temperature (UHT) pasteurized/reconstituted milk 343
- unstable/low persistence foams 261

v

- van der Waals forces 99, 100
- vertical flooding 365
- vesicles
 - characteristics 174
 - polymerized 174–175
 - schematic illustration 173
- votator 345

w

- water in oil (W/O) emulsions 225
- water in oil (W/O) microemulsions 183, 184
- wedge favoring O/W emulsions 234
- wetting
 - agents 363
 - control by surfactants 314
 - and dispersing additives 361–362
 - and related phenomena 308–311
 - cleaning process 314–315
 - detergency and soil removal 314
 - liquid soil removal 317–318
 - nonaqueous cleaning solutions 320–321
 - soil re-deposition 318
 - soil types 315–316
 - solid soil removal 316–317
 - surfactant manipulation 311–314
 - surfactant structure and detergency, correlations of 319–320
- whipped cream 345–347
- Winsor mechanism 197–198

y

- yellow OB dye, solubilization of 193
- yogurts 344
- Young–Laplace equation 101

z

- Ziegler-derived alcohols 30, 69
- Ziegler–Natta catalyst 28
- Ziegler process 36
- zwitterionic surfactants 20, 65, 202